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ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1916.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Applicata	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Apoth.-Zeit.	Apotheker Zeitung.
Arch. Int. Med.	Archives of Internal Medicine.
Arch. Pharm.	Archiv der Pharmazie.
Arkiv. Kem. Min. Geol.	Arkiv för Kemi. Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
Biochem. J.	The Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Gazzetta	Gazzetta chimica italiana.
Gummi-Zeit.	Gummi-Zeitung.
Inter. Zeitsch. Phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Bd. Agric.	Journal of the Board of Agriculture.

* The year is not inserted in references to 1916.

Abbreviated Title.	Journal.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy, Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid-Zeitsch.	Kolloid-Zeitschrift.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. Sci.	Moniteur scientifique de Quesneville.
Nuovo Cim.	Il Nuovo Cimento.
Pharm. J.	The Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Physikal. Zeitsch.	Physikalische Zeitschrift.
P.	Proceedings of the Chemical Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences, Washington.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Soil. Sci.	Soil Science.
Staz. sper. agrar. Ital.	Stazioni sperimentali agrarie Italiani.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Mikroskop.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

In compiling the following Report on progress in the domain of physical chemistry, the practice of previous years has been adhered to, in that the material dealt with may be arranged in a limited number of groups which make no pretence to cover the whole range of the subject. As was to be expected, one of the results of the abnormal conditions is a reduction in the volume of published work; but in spite of the many special claims on the services of those who are normally engaged in scientific research, the past year affords ample evidence of steady progress in many directions.

Elements and Atoms.

The discovery of radioactive disintegration, isotopy, and the simple linear relation between the frequency of the characteristic lines in the *X*-ray spectra of the elements and the atomic number has brought to light a series of facts which are incompatible with the signification attached to the terms element and atom for about a hundred years. The problem of the isotopic elements. which has been the subject of much discussion during recent years,[1] is not only of immediate interest in relation to the periodic system, but has an obvious bearing on certain fundamental ideas which lie at the basis of modern chemical theory.

In radioactive literature, it has been customary to regard isotopes as different elements, but it is doubtful whether this can be justified in a consequential manner. In mass-action effects, whether chemical or electrochemical, they are mutually replaceable, and the tests which ordinarily serve for the recognition of chemical

[1] Compare K. Fajans, *Physikal. Zeitsch.*, 1916, **17**, 1; *A.*, ii, 169. G. von Hevesy and F. Paneth, *ibid.*, 1916, **17**, 4; *A.*, ii, 170.

individuality lead therefore to the conclusion that isotopes are one and the same element.

In a recent paper[2] it is suggested that isotopes should be regarded, not as different elements, but as varieties of one and the same element, which may be defined as a substance which cannot be simplified by any chemical process. Atoms are defined as the ultimate particles which represent the limit of chemical subdivision, and are themselves unchanged by chemical processes.

By reference to these definitions, it is possible to summarise the known facts relating to elements and their isotopic forms in the following statements: (1) the number of the elements is ninety-two, four of which are as yet unknown; (2) each of these elements is characterised by definite chemical and electrochemical properties, by its ordinary and *X*-ray spectra, and by its nuclear change; (3) the atomic weight and radioactive properties are not characteristic constants; (4) the number of varieties of atoms is greater than the number of elements, and up to the present some one hundred and twenty varieties have been identified; (5) an element may be pure or mixed; the constituent atoms of a pure element are similar, whereas a mixed element contains two or more kinds of atoms which differ in weight or in radioactive properties or possibly in respect of both these qualities; (6) in chemical reactions, the active mass of mixed elements is represented by the sum of the active masses of the different varieties of atoms.

In regard to the views summarised in the above statements, it may possibly be objected that the conception of a mixed element is contrary to the fundamental idea implied by the term element, but against this it need only be pointed out that the new conception, like the old, rests on a purely experimental basis. Whether an element is pure or mixed, it represents the ultimate limit of chemical analysis.

Atomic and Molecular Structure.

The introduction of the atomic number hypothesis and the discovery of isotopes have given an impetus to the further study of the relations between the elements, and it has been shown that these recent developments have made it possible to devise a periodic arrangement which expresses the relations between the elements much more perfectly than was possible in the older forms of the periodic table.

Without entering into details, attention may be directed to the interesting papers of Harkins and Hall[3] and of Rydberg,[4] in

[2] F. Paneth, *Zeitsch. physikal. Chem.*, 1916, **91**, 171; *A.*, ii, 240.

[3] W. D. Harkins and R. E. Hall, *J. Amer. Chem. Soc.*, 1916, **38**, 169; *A.*, ii, 241.

[4] J. R. Rydberg, *J. Chim. phys.*, 1914, **12**, 585; *A.*, 1915, ii, 94.

which evidence is put forward in support of an arrangement the essential characteristic of which is a primary grouping of the elements in successive cycles, which contain respectively (1^2), (2^2), 4^2, 6^2, and 8^2 elements, the sequence being determined by the atomic number. Such a grouping is quite probably the expression of some factor which is directly connected with the subatomic architecture.

The suggestion that the nuclei of the higher elements are assemblages of nuclei characteristic of the lower elements was put forward some years ago by Nicholson,[5] and this idea has been further elaborated by Harkins and Hall, who argue that the differences in the atomic masses of elements belonging to the same group are to be attributed entirely to differences in the number of helium nuclei present.

A different view of the nature of the structural units is suggested by van der Broek[6] from a consideration of the numerical relations between the atomic numbers and the atomic weights. Between magnesium (atomic number 12) and thorium (90) there is a difference of sixteen units of atomic weight for a difference of six in the atomic number. The difference of sixteen between the atomic weights of uranium and niton is known to correspond with $4\alpha + 2\beta$ particles, and if the α-particle represents the real constituent of the atoms, this conglomerate would represent the oxygen nucleus (proto-oxygen), the additional 6 β-particles being valency electrons. The fact that the atomic weights are not twice the atomic numbers would then be explained by the formation of these proto-oxygen or θ-particles within the nuclei of the more complex atoms, and the manifestation of radioactivity would be attributable to the disintegration of the θ-particles into the constituent α- and β-particles.

Some experiments[7] on the scattering of X-rays of very short wave-length have shown that equal weights of different elements have the same scattering power. Since the scattering is due to the electrons, this result indicates that the number of electrons in different atoms is proportional to the atomic weight, and in conjunction with previous results it shows that the actual number of electrons is represented by half the atomic weight. The fact that earlier experiments[8] showed a greater scattering power in the case of the heavier elements is in all probability due to the greater

[5] J. W. Nicholson, *Phil. Mag.*, 1911, [vi], **22**, 864 ; *A.*, 1912, ii, 35.

[6] A. van der Broek, *Physikal. Zeitsch.*, 1916, **17**, 260 ; *Nature*, 1916, **97**, 479 ; *A.*, ii, 465.

[7] C. G. Barkla and (Miss) J. G. Dunlop, *Phil. Mag.*, 1916, [vi], **31**, 222 ; *A.*, ii, 282.

[8] C. G. Barkla and C. A. Sadler, *ibid.*, 1908, [vi], **16**, 550.

wave-length of the soft X-rays employed, for in these circumstances the several electrons cannot be assumed to act independently.

An attempt[9] to probe the mechanism involved in chemical change by experiments with model atoms may be briefly referred to. On the assumption that the atoms are spherical in shape and that the electrons revolve in circular orbits, model atoms were constructed from light, hollow, celluloid balls supported in such a way that they were free to rotate about a vertical axis. The revolving electrons were represented by a current passing through a circular coil of wire fastened on to the surface of the sphere at right angles to the equatorial plane. The position of the coil and the direction of the current could be adjusted to correspond with differences in the orbital diameter and the clockwise or anti-clockwise direction of revolution. With the aid of simple models of this kind, it was found possible to determine the conditions of stability in atomic combinations which might be supposed to correspond with molecules of hydrogen, oxygen, ozone, hydrogen chloride, water, hypochlorous acid, chlorine monoxide, and ammonia.

Emission Spectra.

The apparent breadth of what are usually described as sharp lines in the emission spectra of gases has been the subject of much speculation. In the case of lines produced by the action of uncondensed discharges in gases at low pressures, the apparent breadth has been satisfactorily accounted for on the basis of the Doppler effect by taking into account the translatory movements of the radiating centres. This explanation is not, however, in agreement with the observed distribution of the intensity in lines which are emitted under other conditions of excitation. As the result of quantitative measurements on the hydrogen line H_α, and qualitative observations on helium, lithium, and other hydrogen lines, it has been found[10] that the form of the curves, which are obtained by plotting the intensity against the wave-length, is quite inconsistent with the assumption of a single component. These curves show clearly marked discontinuities, and the curvatures of the component curves are all directed away from the axis perpendicular to the wave-length scale, a circumstance which points to the existence of several component lines. These components are supposed to have their origin in the Stark effect, according to which the radiations emitted by a luminous source in a powerful electrical field are resolved into components, the phenomenon being

[9] Sir W. Ramsay, *Proc. Roy. Soc.*, 1916, [*A*], **92**, 451 ; *A.*, ii, 480.

[10] J. W. Nicholson and T. R. Merton, *Phil. Trans.*, 1916, [*A*], **216**, 459 ; *A.*, ii, 461.

analogous to the Zeeman effect in a magnetic field. In the case of H_α, the observed discontinuities in the slopes of the intensity–wave-length curves are in satisfactory agreement with those calculated from the available data relative to the electrical resolution of this line.

Some evidence has been put forward in support of the view that the wave-lengths of certain lines in the arc spectrum of iron vary to a small extent with the length of the arc.[11] If this effect is real, it is of some importance by reason of the fact that lines in the iron arc spectrum have been adopted as secondary and tertiary standards in connexion with the international wave-length scale. The further investigation of the matter[12] has afforded confirmatory evidence of the correctness of the original observation in that the wave-lengths of many lines in the greenish-yellow region have been found to vary slightly with the length of the arc, the strength of the current, and also according to whether the light is emitted from the anode or the cathode. The lines in question, it is true, are all more or less diffuse, but the author contends that the observed displacements are much greater than can be accounted for by unsymmetrical broadening. Although no explanation of the effect has been found, its magnitude is such that it cannot be attributed to variations of pressure within the arc.

Electric Discharge through Gas Mixtures.

Observations on the light emitted by a mixture of gases subjected to the action of direct-current discharge show that the spectrum obtained depends mainly on the relative values of the ionising potentials of the gases in the mixture, and that the relative partial pressures of the gases are of comparatively little importance. If ionised molecules are the luminous centres, it is, of course, to be expected that the spectrum of the most readily ionised gas will be predominant. On the assumption that the intensity of the spectrum of a particular gas is determined by the number of ionised molecules present, theory[12a] indicates that the relative intensities of the spectra of the components of a mixture are mainly dependent on the squares of the ionising potentials.

When a fairly strong current is passed through a tube containing neon mixed with about 10 per cent. of argon, the anode end of the tube shows[12b] the neon spectrum and the cathode end the

[11] F. Goos, *Zeitsch. wiss. Photochem.*, 1911, **11**, 305; *A.*, 1912, ii, 1016.

[12] J. Lang, *ibid.*, 1915, **15**, 223; *A.*, 1916, ii, 65.

[12a] J. Franck and G. Hertz, *Ber. Deut. physikal. Ges.*, 1916, **18**, 213; *A.*, ii, 461.

[12b] F. Skaupy, *ibid.*, 230; *A.*, ii, 469.

argon spectrum. Mixtures of helium and argon behave similarly, and there is evidence to show that the separation of the components of a gaseous mixture under the influence of a direct current is a general phenomenon. If the mixture is introduced at the middle of the discharge tube, and exit tubes are provided in the neighbourhood of the electrodes, it is possible to isolate the separated portions. The behaviour of these mixtures is obviously determined by differences in the magnitude of the ionising potential. Positive ions of the more readily ionised gas are produced by the passage of the discharge, and these move towards the cathode, whilst the non-ionised molecules are constrained to move in the opposite direction under the influence of the resulting difference of pressure.

Absorption Spectra.

In last year's Report some account was given of the application of the quantum theory to the phenomena of selective emission and absorption. Further progress has since been made in the detailed analysis of absorption spectra from this point of view by Baly and his collaborators,[13] and a short account will be given of the results.

According to Baly, the general absorption of any gas depends primarily on certain constants—the so-called basis constants—characteristic of the atoms in the molecule. Each constant is identified with a fundamental frequency given by $\nu_0 = h/2\pi^2 I$, in which h is the Planck constant and I represents the moment of inertia of the particular atom. Corresponding with each fundamental frequency there will be a series of absorption bands, the frequency of which is given by $\nu = hn/2\pi^2 I$, where $n = 1, 2, 3, \ldots$ In each such series the absorptive power will decrease as n increases.

In proceeding from the infra-red to the ultra-violet, sooner or later, a convergence frequency of two of the basis constants is reached, and at this point strong absorption will occur. Corresponding bands will appear at consecutive multiples of this convergence frequency, the intensity decreasing as the higher multiples are reached. In the same manner, intense absorption will occur at the least common multiple of three fundamental frequencies, and there will be a series of bands, equally spaced on the wave-number scale, which correspond with consecutive multiples of this triple convergence frequency.

It has been shown that the ultra-violet and infra-red absorption spectra of sulphur dioxide can be accounted for in a satisfactory manner in terms of three basis constants. One of these is charac-

[13] E. C. C. Baly and C. S. Garrett, *Phil. Mag.*, 1916, [vi], **31**, 512 ; *A.*, ii, 363.

teristic of the sulphur atom and the two others of the oxygen atom.

According to the usual method of description, there are three regions of absorption in the ultra-violet, each characterised by a group of bands with a constant difference in the wave-number, and this difference in frequency is simply related to the basis constants.[14] In the case of the less refrangible ultra-violet band (λ 3182—2802), the constant difference in wave-number is 223·225, corresponding with an infra-red band, which, in accordance with Bjerrum's views, consists of a group of lines the wave-numbers of which are given by $223{\cdot}225 \pm m \times 2{\cdot}73$, in which $m = 1, 2, 3, \ldots$ The centre of the entire system of less refrangible ultra-violet bands corresponds with the wave-number 33751·6, and in accordance with the above views the centres of the series of sub-groups may be expressed by $\nu = 33751{\cdot}6 \pm p \times 223{\cdot}225$, where $p = 1, 2, 3, \ldots$ The observations of Miss Lowater[15] show that the limiting values of p are -7 and $+13$, and of m -44 and $+37$. The complex system of lines, which build up the less refrangible ultra-violet band of sulphur dioxide, consists therefore of twenty-one sub-groups, each containing eighty-two lines. In other words, there are eighty-two series, each of which contains twenty-one lines with a constant difference in wave-number equal to that of the infra-red band ($\nu_0 = 223{\cdot}225$), and the entire system of lines may be represented by the formula $\nu = 33751{\cdot}6 \pm p223{\cdot}225 \pm m2{\cdot}73$. All these lines have not actually been observed, but the general agreement between the observed and calculated frequencies is strongly in favour of the constitution which this formula assigns to the band-group.

The Water Bands.

The changes produced in the infra-red absorption bands of water by the addition of foreign substances have been examined from various points of view. According to the observations of H. C. Jones and his collaborators[16] on aqueous solutions of salts, the effect produced by a salt depends on its affinity for water. Salts which form crystalline hydrates, and are presumably hydrated in solution, cause a diminution in the intensity of the absorption, whilst salts which have little tendency to form hydrates have apparently the opposite effect, although the increase in the intensity is only slight. The general result of this work is in favour of the

[14] Baly and Garrett, *loc. cit.* ; C. S. Garrett, *Phil. Mag.*, 1916, [vi], **31**, 505 ; *A.*, ii, 362.

[15] *Astrophys. J.*, 1910, **31**, 311.

[16] Compare E. J. Schaeffer, M. G. Paulus, and H. C. Jones, *Zeitsch. physikal. Chem.*, 1915, **90**, 561 ; *A.*, 1916, ii, 66.

view that chemically combined water has a smaller absorptive power than water in the free state.

Other observers have found that the presence of foreign substances results in the displacement of the water bands towards the region of greater wave-lengths. This displacement is apparently of the same order for substances of such widely different chemical nature as potassium chloride, hydrochloric acid, and methyl acetate,[17] and is attributed to the formation of additive compounds. In connexion with this method of interpretation, it is noteworthy that the change in the position of the absorption band of pyridine on the addition of water reaches a maximum when the mixture contains equimolar quantities of pyridine and water,[18] a fact which would be most easily explained by attributing the displacement to the formation of a definite compound, C_5H_5N,H_2O. Even if this compound is very appreciably dissociated, its concentration will be a maximum in the mixture referred to.

That the absorption maximum of water is displaced as a result of chemical combination would also seem to be indicated by the results of an investigation of the infra-red absorption of crystalline salt hydrates.[19] In this case, also, the water bands are displaced in the direction of increasing wave-length. Observations made with uniaxial crystals and polarised rays show, moreover, that there is a simple displacement of the maximum when the plane of polarisation is perpendicular to the optical axis, but that a double maximum appears when the plane of polarisation is parallel to the optical axis. The combined water is therefore dichroitic. Similarly, observations made with biaxial crystals show that the combined water is trichroitic, and it would therefore seem that the water of crystallisation in optically anisotropic crystals is itself anisotropic, and that the water behaves optically in accordance with the symmetry relations of the crystalline structure.

Absorption Spectra of the Alkali Haloids.

Aqueous solutions of the haloids of hydrogen and the alkalis have been found [20] to exhibit well-marked selective absorption in the ultra-violet, the position of the head of the band depending only on the haloid element. The frequency of the absorption maximum decreases as the atomic weight of the halogen increases.

[17] R. H. Callow, W. C. M. Lewis, and G. Nodder, *T.*, 1916, **109**, 55; *A.*, ii, 134.

[18] E. C. C. Baly and F. G. Tryhorn, *Phil. Mag.*, 1916, [vi], **31**, 417; *A.*, ii, 278.

[19] C. Schaefer and M. Schubert, *Ann. Physik*, 1916, [iv], **50**, 339; *A.*, ii, 505.

[20] P. J. Brannigan and A. K. Macbeth, *T.*, 1916, **109**, 1277.

Since the selective frequency characteristic of the chlorides differs considerably from that exhibited by gaseous chlorine, and non-ionised organic chloro-compounds show only general absorption, it would seem that the absorption of the haloid salt solutions is due to the chlorine ions. The fact that the molecular extinction coefficient increases with increasing concentration of the solution shows, however, that the ions of themselves are not responsible for the absorption, and in explanation of the observations it is suggested that the selective absorption is due to vibrations set up in the halogen ions by the specific action of the metal ions. In agreement with this hypothesis, it is found that the molecular extinction coefficient for the chlorides and iodides increases with the atomic weight of the associated metal.

Equations of State.

The success achieved by the van der Waals's equation in its application to the interpretation of the behaviour of gases is largely responsible for the comparative neglect of more recent attempts to explain the pressure–volume–temperature relations of fluids. The neglect is real and quite unjustifiable, and for this reason the writer would direct attention to a very interesting analysis[21] of the Dieterici equation,[22] which leads the author to the conclusion that this equation is not only in better agreement with experiment, but rests on a sounder theoretical basis than the equation of van der Waals.

In the Dieterici equation the relation between the boundary pressure p and the pressure within the fluid π is given by $p=\pi e^{-A/RT}$, in which A represents the work done by the molecules in penetrating to the surface. On the assumption that A is proportional to the density of the fluid or $A=a/v$, the equation assumes the form $p=RT/v-b \,.\, e^{-a/vRT}$.

At low pressures, when v is large, the equation may be written $p=\frac{RT}{v-b}(1-a/vRT)=RT/(v-b)-a/v(v-b)$, which is virtually identical with the van der Waals's equation. At higher pressures there is, however, a very considerable difference between the two equations, and the superiority of the Dieterici equation in this region is shown very clearly in its representation of the critical relations.

The Dieterici isothermals are of the same type as those of van der Waals, and at temperatures below the critical temperature and pressures which are not far removed from the pressure of the satur-

[21] F. H. MacDougall, *J. Amer. Chem. Soc.*, 1916, **38**, 524 ; *A.*, ii, 215.

[22] C. Dieterici, *Ann. Physik*, 1901, [iv], **5**, 51.

ated vapour there are three values of v on the theoretical curves. When the pressure is equal to the saturated vapour pressure, two of these correspond with the volumes of the liquid (v_1) and the saturated vapour (v_2), whilst the third (v_3) corresponds in reality to a state in which both liquid and vapour are present.

If the pressure of the saturated vapour is denoted by p_s, then

$$p_s = \frac{RT}{v_1 - b} e^{-a/v_1 RT} = \frac{RT}{v_2 - b} e^{-a/v_2 RT} = \frac{RT}{v_3 - b} \cdot e^{-a/v_3 RT}.$$

On the assumption that the third point on the theoretical isothermal corresponds with a density which is the arithmetic mean of the densities of the liquid and the saturated vapour or $2/v_3 = 1/v_1 + 1/v_2$, it may easily be shown that the above equations lead to the relations:

$$v_3 = 2b \quad \text{and} \quad 1/b = 1/v_1 + 1/v_2,$$

and it follows that the pressure of the saturated vapour is given by

$$p_s = \frac{RT}{b} e^{-a/2bRT}.$$

which may be written in the form:

$$p_s = (d_1 + d_2) RT e^{-a(d_1+d_2)/RT},$$

where d_1 and d_2 are the densities of the liquid and saturated vapour respectively.

In favour of the assumption $2/v_3 = 1/v_1 + 1/v_2$, it is pointed out that all three values of v become equal to $2b$ at the critical temperature, and that it is plausible to assume that the law of Cailletet and Mathias has actual reference to the third point on the theoretical isothermal. Further support is afforded by the fact that the geometric mean of the maximum and minimum pressures on any theoretical isothermal is equal to $\frac{RT}{b} e^{-a/2bRT}$, which is the calculated pressure of the saturated vapour if $v_3 = 2b$. It is argued that this result is not a chance mathematical agreement, but that it corresponds with some physical reality the nature of which becomes evident if the above assumption is accepted.

For various substances, values of a and b have been calculated from Young's data, and in all cases it is found that a and b are functions of the temperature. For *iso*pentane, fluorobenzene, *n*-hexane, and carbon tetrachloride, a decreases and b increases up to the critical temperature. Above the critical temperature, the data for carbon dioxide and ethylene show that a decreases whilst b remains nearly constant, whilst in the case of hydrogen a and b both decrease as the temperature rises.

In view of this dependence of a and b on the temperature, the Dieterici equation does not reproduce the actual behaviour of any

fluid accurately, but, as McDougall's analysis shows, it certainly merits more serious attention than it has hitherto received.

In a recent criticism[23] of the van der Waals's equation, arguments are advanced in favour of the alternative formula,

$$p+a/(v+b)^2=RT/v.$$

Analysis of this equation in its application to the critical condition leads to the conclusion that the internal pressure, p_c, is equal to the external pressure, P_c. Denoting the total pressure by π_c, we have then:

$$p_c=P_c=RT_c/2v_c \quad \text{and} \quad \pi_c=RT_c/v_c.$$

According to the last equation, the relation between the total pressure, volume, and temperature is given by the ideal gas equation.

The equality of p_c and P_c is supposed to be intimately connected with the disappearance of the surface tension and the latent heat of vaporisation at the critical point. In this condition the cohesive forces are exactly counterbalanced by the thermal pressure, and the transference of a molecule from the liquid to the vapour requires no expenditure of energy.

Apropos of the critical phenomena it may be noted that no trace of critical opalescence has been met with in experiments[24] on gases of low critical temperature, such as oxygen, nitrogen, carbon monoxide, and methane. Although the emulsion theory affords no explanation of these facts, it is claimed that the apparent absence of the effect at low temperatures is consistent with Smoluchowski's theory that the opalescence is due to a lack of homogeneity resulting from inequalities in the distribution of the molecular velocities. Maxwell's distribution formula, in fact, leads to the conclusion that the velocities of the molecules will tend towards a uniform value with lowering of the temperature, and local differences in density will consequently become less pronounced as the critical temperature falls.

Additive Relations of b *and* $\sqrt{a}$.

By comparing the van der Waals's constants for a large number of substances in the critical condition, van Laar has found[25] that additive relations are exhibited by b and $\sqrt{a}$. Atomic constants have been derived for a number of elements, from which it is possible to calculate the values of a and b for any substance containing these elements.

The approximately additive character of b has, of course, been

[23] J. Kam, *Phil. Mag.*, 1916, [vi], **31**, 22; *A.*, ii, 174.

[24] E. Cardoso, *J. Chim. phys.*, 1915, **13**, 414; *A.*, 1916, ii, 216.

[25] J. J. van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1220; *J. Chim. phys.*, 1916, **14**, 3; *A.*, ii, 386.

recognised from the time when the theory of corresponding states indicated the conditions under which the molecular volumes of different substances were to be compared, and since the ordinary boiling points are approximately corresponding temperatures, the additivity of b may be said to have been demonstrated by Kopp's system of molecular volumes. As in previous attempts to derive atomic constants, van Laar finds it necessary to suppose that the value of b for certain elements (hydrogen, carbon, nitrogen, and oxygen) depends on the nature of the other elements with which these are combined. If, however, what are termed the fundamental values are considered, it appears that b is a periodic function of the atomic weight. In the carbon, nitrogen, oxygen, and fluorine groups there is a constant difference between the values of b for adjacent homologues, and also for the adjacent elements in each horizontal series.

Of greater interest is the evidence furnished in support of the additive character of $\sqrt{a}$. The atomic constants derived from the elements of the above-mentioned groups are very simply related, in that the elements in each horizontal series have the same value of $\sqrt{a}$, whilst the values for the successive horizontal series form an arithmetic progression.

The most important result obtained is the demonstration that the tervalent atoms of nitrogen and phosphorus and the quadrivalent atoms of carbon, germanium, and tin are of no account in determining the magnitude of the attraction constant when the atoms in question are combined respectively with three or four univalent atoms or groups. In these circumstances, the ter- and quadri-valent atoms exert no influence on the attractive forces between the molecules of which they form the nucleus.

The view [26] that the attractive constant is determined by the molecular weight (M) and the number of effective valencies (n) as expressed by the equation $a = c(Mn)^{\frac{3}{2}}$, is obviously inconsistent with the additivity of $\sqrt{a}$.[27]

New methods for the derivation of the values of a and b for the metallic elements are also discussed [28] by van Laar. The attraction constants obtained for mercury and antimony from data for the corresponding halogen compounds lead to the conclusion that the free elements in the condition consist of complex molecules, the molecule of mercury containing two atoms and the molecule of antimony about twelve atoms. By similar reasoning, it follows that

[26] A. P. Mathews, *J. Physical Chem.*, 1913, **17**, 183; *A.*, 1913, ii, 414. Compare also *ibid.*, 1916, **20**, 554; *A.*, ii, 600.

[27] J. J. van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1235; *A.*, ii, 387.

[28] *Ibid.*, 1916, **19**, 2; *A.*, ii, 610.

elements which, like carbon, have a very high critical temperature and a comparatively small attraction constant, must consist in the critical condition of molecules which contain a very large number of atoms. Assuming that the critical temperature of carbon is 6000°, the calculated number of atoms in the molecule is 80.

Since the critical temperature is connected with the attraction constant by the equation $T_c = 78a/b$, it follows that substances such as methane, carbon tetrachloride, stannic chloride, and ammonia will have relatively low critical temperatures and will be more volatile than they would be if the central atoms contributed towards the magnitude of the intermolecular attractive forces.

Vapour Pressures of Binary Mixtures.

The interpretation of results obtained in recent work on the connexion between the vapour pressure and the composition of binary liquid mixtures has, to a large extent, centred round the view, advocated more particularly by Dolezalek,[29] that the partial pressures of the components of a normal mixture are determined by the molar fractions of the components in the mixture in accordance with the equations $p_A = xP_A$ and $p_B = (1-x)P_B$, where P_A and P_B are the vapour pressures of the pure components and p_A and p_B the corresponding partial pressures in a mixture containing A and B in the molar ratio $x:1-x$; and, further, that deviations from the requirements of these equations afford indications of chemical combination between the components or of changes in the degree of molecular complexity.

These equations, it may be noted, are identical with the empirical relation established in an approximate manner by Raoult for mixtures in which one of the components is non-volatile, and their acceptance as a basis for the interpretation of vapour-pressure curves involves the assumption that the vapour pressures of mixtures are independent of the intermolecular forces, in so far as these do not lead to changes in the molecular condition, either by polymerisation, dissociation, or chemical combination. So long as the problem is considered from the point of view of the molecular theory, it seems difficult to deny that many properties of such mixtures must depend on the magnitude of the forces acting between the molecules, that is to say, on the molecular environment, and for this reason many physical chemists have hesitated to accept the assumption which underlies the above-mentioned theory. None the less, it must be recognised that some chemists have been led to regard as quite plausible the interpretation which has been given

[29] *Zeitsch. physikal. Chem.*, 1908, **64**, 727; *A.*, 1909, ii, 22; *ibid.*, 1910, **71**, 191; *A.*, 1910, ii, 184; *ibid.*, 1913, **83**, 40; *A.*, 1913, ii, 481.

by Dolezalek and others of their investigations of the properties of binary liquid mixtures.

To obtain further light on the questions at issue between Dolezalek and van Laar, who has consistently opposed the application of the simple mixture rule in the interpretation of property–composition curves, measurements have recently been made[30] of the vapour pressures of mixtures of non-electrolytes, one component of which is not appreciably volatile at the temperature of the experiments. The combinations were chosen so as to include pairs of normal liquids, pairs of associated liquids, and pairs in which one component is normal and the other associated. It is said that the experimental data can be adequately explained in a qualitative way by the assumption that the form of the vapour pressure curve is determined by molecular changes, but that Dolezalek's theory does not afford a satisfactory basis for a quantitative explanation.

An equation connecting the vapour pressure and the composition of binary mixtures has been derived by the application of the Dieterici equation of state to such mixtures.[31] The equation, which is identical in form with van Laar's thermodynamic formula, may be written:

$$p = p_1 x e^{-(A_1' - A_1)/RT} + p_2(1-x)e^{-(A_2' - A_2)/RT}.$$

in which p_1 and p_2 are the vapour pressures of the pure components X and Y, A_1 and A_2 the work done when a molecule of X or Y is evaporated from the pure liquids, A_1' and A_2' the corresponding work done when evaporation takes place from the mixture containing X and Y in the molar ratio $x:1-x$. The quantities $(A_1' - A_1)$ and $(A_2' - A_2)$ represent very nearly the differences between the molecular heats of vaporisation of the components in the mixture and the corresponding latent heats for the pure liquids, and by a simple transformation it may be shown that the deviation of the vapour pressure from the straight line law is determined by the magnitude of the difference between the two heats of vaporisation. If the actual heat of vaporisation is greater than that calculated from the mixture rule, the vapour pressure will be less than that corresponding with the straight line relation, and vice versa.

Although the thermal data required to test this conclusion are not available, the close parallelism between the surface tension and the latent heat affords an indirect method, and in this connexion it has been pointed out[32] that the vapour pressures of binary mixtures are greater, equal to, or less than those calculated from the mixture rule according as the surface tensions are less, equal to, or

[30] F. H. Campbell, *Trans. Faraday Soc.*, 1915, **11**, 91; *A.*, 1916, ii, 83.
[31] F. Tinker, *Phil. Mag.*, 1916, [vi], **32**, 295; *A.*, ii, 516.
[32] F. P. Worley, *T.*, 1914, **105**, 273.

greater than those calculated from the formula $\gamma = v_1\gamma_1 + v_2\gamma_2$, in which v_1 and v_2 are the practical volumes of the components.

The above conclusion relative to the connexion between the vapour-pressure curve and the latent heat of vaporisation has been reached independently [33] by theoretical reasoning based on the use of the van der Waals's equation, and in this paper attention is directed to the fact that the mixing of normal liquids is accompanied by heat absorption, and that, consequently, the vapour pressures of normal mixtures will be greater than those calculated from the mixture rule.

Preference is also given to the equation of state as a basis for the interpretation of the vapour pressures of mixtures in an interesting paper [34] by J. H. Hildebrand. The idea is again put forward that the validity of Raoult's law is probably limited to mixtures in which the forces acting between the molecules are not very different from those acting between the molecules of the pure liquids and approximate equality of the internal pressures is suggested as a criterion for the required similarity in the molecular environment. The internal pressure is not, however, the only factor of importance, and attention is directed to the very important part which seems to be played by the polarity of the molecules. Electrically polar molecules will tend to form associated groups, giving rise to increased internal pressure and surface tension, and in consequence of the orientation of the molecules in an electrical field, the polarity will be associated with a high dielectric constant.

Examples of polar liquids are furnished by the ionising solvents, by molten salts which are known to be characterised by abnormally high values of surface tension and association factor, and by the molten metals in which the polarity attains its highest development, this being associated with high surface tension and also with high electrical conductivity.

Whenever one or both of the components of a mixture are polar in the sense referred to, deviations from Raoult's law are to be expected, and by reference to data for the solubility of gases in liquids, the miscibility of liquid pairs and the solubility of solids in liquids, the author seems to make out a good case for the consideration of the polarity as an important factor in the determination of the molecular environment and indirectly of the properties of mixtures.

[33] R. Kremann, *Monatsh.*, 1916, **37**, 369 ; *A.*, ii, 515.

[34] J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1916, **38**, 1452 ; *A.*, ii, 518.

Other Properties of Binary Mixtures.

A glance at the literature relating to property–composition curves gives the impression that, in most cases, the components are chosen in a more or less haphazard fashion, although it is obvious that the comparative investigation of groups of similar substances may lead to information of considerable value for the interpretation of property–composition curves. This factor has been kept in view in a recent investigation, in which the density,[35] viscosity,[35] heat of reaction,[36] and the specific heat[36] of mixtures of phenols of varying degrees of acidity with organic bases of different strengths have been systematically examined and the data compared with the indications afforded by freezing-point measurements.[37] A priori, it is to be expected that the acid and basic components of such mixtures will combine to form more or less stable, salt-like compounds, and, further, that this will depend on the strength of the acid and the base.

In most cases, the freezing-point determinations indicate the formation of 1 : 1 compounds, and the only mixtures for which there is no evidence of chemical combination, are those which contain a very weak base.

When the freezing-point curves are compared with the viscosity–composition curves, both sets of observations lead to the same conclusion in some cases, but in others they are apparently not in agreement. For pairs of substances in which the freezing-point diagram definitely shows that a solid compound is formed, the composition corresponding with maximum deviation from the mixture rule is frequently found to diverge very appreciably from that of the compound. The author ascribes this to the disturbing influence of changes in the molecular complexity of the components and to their unequal dissociating power, and on this account it is said that the viscosity–deviation curves cannot be regarded as a trustworthy test of compound formation, and still less can they be regarded a affording a safe means of determining the composition of such compounds.

With one exception, the mixtures of phenols and bases show considerable development of heat on mixing. The mixture which corresponds with the maximum heat development is not, however, in most cases the 1 : 1 mixture, and this divergence is again ascribed to changes in the molecular complexity of the components. Such changes also complicate the interpretation of the specific heat curves, and it would seem doubtful whether any of these properties

[35] A. Bramley, *T.*, 1916, **109**, 10 ; *A.*, ii, 125 ; *T.*, 1916, **109**, 434 ; *A.*, ii, 376.
[36] *Ibid.*, 496 ; *A.*, ii, 372. [37] *Ibid.*, 469 ; *A.*, ii, 371.

can be made use of in a general way in the elucidation of the constitution of binary liquid mixtures.

In the writer's opinion this is not entirely or even mainly due to the disturbing influence of changes in the molecular complexity of the components, but to the incorrectness of the assumption that the simple mixture rule is characteristic of mixtures in which there is neither chemical combination nor molecular dissociation. As a basis for the interpretation of property–composition curves, the straight line law is perhaps attractive on account of its simplicity, but this must not be confused with the plausibility of the hypothesis. The degree of plausibility will depend on the property considered, but in actual practice the hypothesis has been used in the interpretation of curves obtained by plotting all kinds of properties against the composition with practically no regard for the physical meaning of the curves. These methods of dealing with experimental observations are bound to reveal inconsistencies, and in many cases to lead to fallacious conclusions.

Additive Compounds of Organic Acids.

At this point, reference may conveniently be made to results obtained in the investigation of the freezing points of pairs of organic acids,[38] which show that additive compounds are formed when the strengths of the acids are widely separated. Oxonium compounds of the same type are also formed by the union of phenols with organic acids [39] if the difference between the acidic strengths is sufficiently pronounced. Thus, phenol and its alkyl derivatives form compounds with trichloroacetic acid and also with trinitrophenol.

By the same method it has been found that organic acids combine with esters,[40] and that combination is most marked between strong acids and the esters of weak acids. The readiness with which combination occurs decreases rapidly with decrease in the strength of the acid, but the phenomenon appears to be characteristic of ester–acid systems. These observations are obviously significant, in view of the fact that ester hydrolysis under the catalytic influence of acids is usually attributed to the formation of intermediate additive compounds.

[38] J. Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1722; *A.*, 1914, 1, 1069; compare also *ibid.*, 1914, **36**, 1222; *A.*, 1914, i, 858; *ibid.*, 1915, **37**, 149; *A.*, 1915, i, 80.

[39] *Ibid.*, 1916, **38**, 1309; *A.*, i, 599.

[40] J. Kendall, and J. E. Booge, *ibid.*, 1712; *A.*, i, 707.

Osmotic Pressure.

In continuation of the well known investigations of Morse and Frazer, further observations have been made[41] on the osmotic pressure of solutions of sucrose with a new form of apparatus adapted to the study of concentrated solutions, in which osmotic equilibrium is attained after a few hours. In this apparatus the porous cell containing the solvent is surrounded by a metal cylinder containing the solution and connected with a manometer. The copper ferrocyanide membrane is deposited on the outer surface of the porous cell, and the equilibrium pressure, which is developed, as in the original form of apparatus, by the action of the osmotic forces, is measured by means of an electrical resistance gauge. The indications of this gauge depend on the fact that the resistance of certain metallic conductors increases in an approximately linear manner with the external pressure. The gauge coil was made of "Thirlo" wire, an alloy of copper, manganese, and aluminium with a very low temperature-coefficient ($+0{\cdot}0000056$ per degree), a negligibly small thermoelectric effect against copper and a pressure-coefficient of about two parts per million per atmosphere, and this enabled measurements to be carried out with an accuracy of 0·1 atmosphere over a range of five hundred atmospheres.

The results obtained at 30° are in remarkably close agreement with those recorded by the Earl of Berkeley and E. G. J. Hartley,[42] as is evident from the following table, in which the data of these observers are reduced from 0° to 30° by the use of the ordinary gas coefficient:

Grams of sucrose per litre	180·1	300·2	420·3	540·4	660·5	750·6	
Grams of sucrose per 1000 grams of water	202·0	370·0	569·0	820·0	1133·0	1430·0	
Osmotic pressure (F. and M.)	15·59	29·78	47·88	73·06	109·1	148·8	atm.
Osmotic pressure (B. and H.)	15·48	29·72	48·81	74·94	111·87	148·46	atm.

The whole series of measurements, which extends to a pressure of about 270 atmospheres, shows that the ratio of the osmotic pressure to the weight concentration of the sucrose approximates to a constant value as the concentration approaches that of the saturated solution.

By neglecting the compressibility of the solutions and calculating the osmotic pressure from the formula $P = RT/V_0 . \log N + n/N$, in which N and n are the respective mol. numbers of water and

[41] J. C. W. Frazer and R. T. Myrick, *J. Amer. Chem. Soc.*, 1916, **38**, 1907; *A.*, ii, 603.

[42] *Proc. Roy. Soc.*, 1904, **73**, 436.

sucrose and V_0 is the molar volume of the solvent, on the assumption that the association factor of water is equal to two, it is found that the differences between the observed and calculated osmotic pressures cannot be explained by postulating the formation of molecular aggregates containing either five [43] or six [44] molecules of water per molecule of sucrose. To bring the facts into line with the above formula it seems necessary to assume that the number of molecules of water of hydration decreases continuously from about six in the less concentrated solutions to about four in the case of the nearly saturated solution.

It may also be noted that recent measurements [45] of the vapour pressures of concentrated solutions of sucrose (60 to 70 per cent. sucrose) at temperatures between 60° and 90° lead to the conclusion that each molecule of sucrose is combined with about four molecules of water. The degree of hydration seems to decrease slightly with rise of temperature.

Further determinations of the osmotic pressure of sucrose solutions by the English experimenters [46] have given values for the more dilute solutions which are smaller than those recorded by the American observers to an extent which cannot be accounted for by the probable errors of the experiments. The discrepancy increases with the dilution, as shown by the following numbers, which give the concentration of the solution (grams of sucrose per 100 grams of water) and the percentage difference between the two series of osmotic pressures: 33·9, 0·1 per cent.; 30·6, 0·2 per cent.; 20·5, 1·2 per cent.; 10·2, 2·4 per cent.; 3·39, 8·2 per cent.

For the approximate measurement of small osmotic pressures, a simple dynamic method is described in which rates of osmotic flow are compared. If the rate of flow for a standard substance of molecular weight M at concentration c is R, and the corresponding quantities for a second substance are M_1, c_1, and R_1, then M_1 may be obtained with an accuracy of about 2 per cent. from the relation $M_1R_1/c_1=MR/c$.

Structure of Semipermeable Membranes.

The microscopic examination of various kinds of semipermeable membranes has shown [47] that the structure is distinctly granular and that the size of the granules varies considerably from one sub-

[43] R. L. Callendar, *Proc. Roy. Soc.*, 1908, [*A*], **80**, 466; *A.*, 1908, ii, 671.
[44] E. W. Washburn, "Principles of Physical Chemistry," 1915.
[45] D. O. Wood, *Trans. Faraday Soc.*, 1915, **11**, 29; *A.*, 1916, ii, 82.
[46] Earl of Berkeley and E. G. J. Hartley, *Proc. Roy. Soc.*, 1916, [A], **92**, 477; *A.*, ii, 518.
[47] F. Tinker, *ibid.*, 357; *A.*, ii, 298.

stance to another, the diameter ranging from 0·1 to 0·4 μ for copper ferrocyanide and Prussian-blue, from 0·5 to 1·0 μ for peptone tannate, and from 3 to 4 μ for silver chloride and barium sulphate. These granules are aggregates of the ultra-microscopic particles which are present in the corresponding sols, these particles being, however, more closely knit together than in an ordinary gel.

The fact that those membranes which have the smallest pores, namely, copper ferrocyanide and Prussian-blue, are the most efficient semipermeable diaphragms, shows that the osmotic properties are not due to any selective blocking action, but that there is a close connexion between the osmotic activity and the extent to which the membrane capillaries are under the control of surface forces. The relations may be interpreted on the assumption that the osmotic effects are due to selective adsorption at the surface of and in the capillaries of the membrane, the diaphragm being impermeable to those substances which are negatively adsorbed.

Certain anomalous, although apparently well-established, cases of osmosis have been described, in which either the solutions separated by the semipermeable membrane are isosmotic or in which the flow of water is from the solution of greater to that of lower osmotic pressure (negative osmosis). It is suggested [48] that these effects are due to electro-endosmose under the influence of local electric currents which are set up when the membrane is not only permeable to the solvent, but also to certain electrolytes or particular ions. The Becquerel phenomenon is in the same way attributable to electrostenolysis under the influence of local currents.

Colloidal Solutions.

The nature of the electrical process for the production of colloidal solutions of the metals has not yet been satisfactorily explained. On the one hand, it has been suggested that the disintegration is a thermo-mechanical process, and on the other that the effects are essentially electrolytic.

There seems to be no doubt, however, that the electrical dispersion of metals in conductivity water is accompanied by an appreciable increase in the conducting power of the solution. If the charge on the particles is derived from Stokes's formula, and this, in combination with the number, size, and mobility of the particles is used in the calculation of the increase in the electrical conductivity of the solution, it is found that the observed increase is many thousand times greater than the calculated value. Recent

[48] H. Freundlich, *Kolloid Zeitsch.*, 1916, **18**, 11 ; *A.*, ii, 227.

experiments[48a] on gold and platinum sols show that the increase is much greater for platinum than for gold, and that the platinum solutions are much more stable. The differences are said to have their origin in the greater readiness with which the platinum is oxidised during the discharge, the anions thus formed being essential for the stability of the solutions. In support of this view, it has been found that the presence of certain anions (chlorine, bromine, iodine, hydroxyl) in the original liquid has a very marked influence on the stability of the resulting solutions. The stabilising effect is not obtained, however, if the metal is dispersed in pure water and the electrolyte added subsequently. The conclusion drawn from these experiments is that the electrical process of dispersion consists in a primary thermochemical disintegration followed by the combination of the highly disperse metal with ionised oxidation products, with the result that negatively charged colloidal complexes are produced.

In a further attempt[49] to explain the above-mentioned discrepancy between the observed and calculated conductivities of electrically prepared metallic sols, it is suggested that the colloidal particles adsorb both cations and anions, but that these are differently distributed in the ionic envelope. In passing from the particle outwards along the radius of the envelope, the concentration of each ion decreases, but the curves representing the distribution are not superposable. The inner layers have an excess of the one ion and the outer layers an excess of the opposite kind. The two intersecting curves ultimately become coincident when the region of normal ionic distribution is reached. On this view, it is not possible to calculate the electrical charge on the basis of Stokes's law, for there is no charge in the usual sense.

According to Einstein's formula, the relation between the viscosity, η, of a colloidal solution and the viscosity, η_0, of the dispersive medium is given by $\eta = \eta_0(1 + 5/2\phi)$, in which ϕ represents the fraction of the total volume occupied by the disperse phase. This simple relation is of particular interest in view of the frequent application of viscosity in the investigation of the changes which occur in colloidal solutions under the influence of time or of foreign substances, whether exerting a coagulating or a protective effect. The formula has not been generally accepted, however, and the fact that coagulation is usually accompanied by an increase in viscosity is supposed to be entirely at variance with Einstein's equation, which requires that the viscosity shall be independent of the size of the particles.

[48a] H. T. Beans and H. E. Eastlack, *J. Amer. Chem. Soc.*, 1915, **37**, 2667; *A.*, 1916, ii, 89. [49] F. Powis, *Trans. Faraday Soc.*, 1916, **11**, 160; *A.*, ii, 408.

In a recent theoretical discussion of the viscosity of colloids,[50] it is pointed out that the observed increase in viscosity is not necessarily contrary to the above formula, since it must be shown that the colloidal solutions satisfy the conditions which were assumed in the derivation of the formula. The formula is, in fact, only applicable to solutions in which the particles are spherical. If coagulation results in the formation of non-spherical aggregates, an increase in the viscosity is to be expected, and even if the aggregates are approximately spherical, it may be shown that the total volume of the coagulated particles must be at least $3\sqrt{2}/\pi = 1{\cdot}35$ times as large as that of the non-coagulated particles, and this, according to the formula, would result in an increased viscosity. Apart from this, the formula is not applicable to highly disperse colloids, for the underlying theory involves the assumption that the radius of the particles is very large in comparison with the radius of molecular action. To bring the observed behaviour of highly disperse colloids into line with the formula, it has been suggested[51] that each particle is surrounded by an envelope of dispersive medium (adsorption film), but in the author's opinion there is no clear evidence of the existence of such envelopes. A further restriction on the range of applicability of the formula is that the value of ϕ must not be too large. If the concentration is such that the radius of the particles of the disperse phase is no longer small in comparison with the mean distance between them, it can be shown that the influence of ϕ on the viscosity should be represented by a formula containing higher powers of ϕ.

The Einstein formula has been criticised by Hardy, but his main objections seem to be met by the statement[52] that neither this nor any other formula representing the viscosity of colloidal solutions is applicable to systems which in many respects approximate in their behaviour to elastic solids.

Doubly Refracting Colloidal Solutions.

Under certain conditions, colloidal solutions of vanadium pentoxide exhibit double refraction and resemble crystalline liquids.[53] If such a solution is made to flow through a tube fitted at the ends with crossed Nicols, the field of view in convergent light is illuminated and shows the cross and concentric rings characteristic

[50] M. von Smoluchowski, *Kolloid Zeitsch.*, 1916, **18**, 190 ; *A.*, ii, 473.

[51] E. Hatschek, *Zeitsch. Chem. Ind Kolloid*, 1912, **11**, 280, 284 ; *A.*, 1913, ii, 122.

[52] E. Hatschek, *Proc. Physical Soc. London*, 1916, **28**, 250 ; *A.*, ii, 420.

[53] H. Diesselhorst and H. Freundlich, *Physikal. Zeitsch.*, 1915, **16**, 419 ; *A.*, 1916, ii, 65.

of a plate of a uniaxial crystal cut perpendicularly to the axis. If the tube is of triangular cross-section and is used as a prism, the red hydrogen line is resolved into two oppositely polarised lines, the more strongly refracted of which has its vibrations parallel to the direction of flow.

The double refraction is also observed when the solution is subjected to the action of an electrical or magnetic field.[54] If the electrical field is parallel to the direction of the convergent luminous beam, there is very little dispersion and the particles seem to disappear, but if the field is perpendicular to the light rays, the Tyndall effect is very pronounced.

It is quite clear that the colloidal particles are elongated and undergo orientation under the influence of external agencies, but in regard to the cause of the double refraction, whether this is due to the anisotropic character of the particles themselves or to directional differences in the elastic properties of the solution as a whole, there have been differences of opinion. According to Freundlich,[55] the elongated particles consist of clusters of similarly directed molecules forming a link between the amorphous and crystalline states. This, however, is not in accord with more recent observations,[56] which point strongly to the view that the sol particles are micro-crystalline. It has, in fact, been found that a freshly prepared vanadium pentoxide sol is isotropic and shows no trace of double refraction; on keeping the solution, however, it becomes gradually doubly refractive, and at the same time there is a perceptible increase in the size of the ultra-microscopic particles.

Experiments made with other substances, which are usually deposited in the form of micro-crystals, show that these may be obtained as doubly refracting sols when the conditions of formation are suitably modified. In this way, solutions of mercurous chloride and lead iodide have been prepared, the properties of which are quite similar to those of vanadium pentoxide sol. It would therefore seem that the anisotropy of colloids is to be referred to the crystalline nature of the particles.

Some remarkable variations have been found[57] in the properties of aqueous solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid when the concentration is changed. In dilute solution the acid behaves like an ordinary electrolyte, but as the concentration increases, the solution becomes more and more colloidal in nature,

[54] H. R. Kruyt, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1625; *A.*, ii, 486.

[55] *Zeitsch. Elektrochem.*, 1916, **22**, 27.

[56] W. Reinders, *Proc. K. Akad. Wetensch. Amsterdam.*, 1916, **19**, 189; *A.*, ii, 589.

[57] H. Sandqvist, *Kolloid Zeitsch.*, 1916, **19**, 113; *A.*, ii, 556.

and ultimately a third stage is reached in which it becomes anisotropic and resembles the crystalline liquids in its general properties. Fall of temperature has the same effect as increase of concentration, and the same series of changes is brought about by the addition of a strong mineral acid. In the intermediate phase, the electrical conductivity of the acid is approximately normal, although the viscosity of the colloidal solution increases very rapidly with the concentration. In contrast with ordinary colloidal solutions, the properties of solutions of this acid appear to be completely determined by the concentration, temperature, and foreign substances present, and independent of the previous history. The transition from the isotropic to the anisotropic condition takes place, moreover, at a perfectly definite temperature, dependent only on the concentration of the acid and on the nature and quantity of foreign substances present.

Coagulation of Colloids.

The fact that hydrocarbon oil emulsions are coagulated when the difference of potential falls below a certain critical value was referred to in the Report for the year 1915 as affording evidence against the view that coagulation occurs only when the isoelectric condition is reached. Further observations[58] on colloidal solutions of arsenious sulphide have given similar results, and thus there are grounds for the assumption that the critical potential is a factor of general import in connexion with the coagulation of colloids.

Emulsification and Detergent Action.

In the interpretation of the results of a systematic investigation[59] of the changes in surface energy at the surface of contact of acid, neutral and alkaline solutions of potassium oleate with pure benzene and with benzene containing free fatty acid, it is shown that a satisfactory explanation of the stalagmometric data can only be obtained on the assumption that the detergent action is due to the formation of a quasi-solid surface layer of colloidal soap. This may be produced by interaction of the alkali in the aqueous solution and the free fatty acid in the benzene, or may be directly adsorbed from the aqueous solution. In the ordinary use of soap solution as a detergent, both actions come into play, for the solutions are appreciably hydrolysed. The two effects are not additive, however, for the surface activity of "hydrolysis"

[58] F. Powis, *T.*, 1916, **109**, 734; *A.*, ii, 523.

[59] S. A. Shorter and S. Ellingworth, *Proc. Roy. Soc.*, 1916, [A], **92**, 231; *A.*, ii, 130.

alkali is apparently less than that of the same quantity of free alkali, whilst the activity of the soap is increased in presence of alkali. This increase cannot be accounted for by the suppression of hydrolysis, and the authors suggest that the effect may be due to an increase in the colloidal nature of the semi-colloidal soap solution.

Rotation Dispersion and Dynamic Isomerism.

In the Annual Report for 1914 an excellent summary was given of recent work on rotation dispersion, and in particular of recent attempts to explain the phenomenon of anomalous rotatory dispersion. The hypothesis that this effect is due to the presence of isodynamic forms of opposite rotation and unequal dispersion is subjected by T. S. Patterson to a searching criticism,[60] which suggests that the enthusiasm with which this idea has been taken up in certain quarters is not well founded.

The view that liquids exhibiting anomalous rotatory dispersion contain two different substances dates back, of course, to the middle of last century, and the novelty of Armstrong and Walker's theory[61] lies in the suggestion that these are isodynamic forms, and that all substances which show a variable rotation with change in the external conditions, independently of whether they show normal or anomalous dispersion, are to be regarded as equilibrium mixtures of isomeric forms, the rotation and dispersion of which are fixed and unalterable. The hypothesis involves the negation of all temperature and solvent effects in the ordinary sense, the actually observed variations of rotation being referred to changes in the relative proportions of the isomerides due to a displacement of the equilibrium.

As evidence against the correctness of this hypothesis, Patterson puts forward the case of nitrocamphor, which is known to undergo changes in rotation at a conveniently slow and measurable rate as the result of isodynamic change. The initial rotation of α-nitrocamphor in 5 per cent. solution in benzene, xylene, and chloroform is $-125°$, $-99°$, and $-27°$ respectively; after equilibrium has been attained the corresponding rotation values are $-104°$, $-73°$, and $-15°$. The initial rotation of α-nitrocamphor in any one of these solvents varies, moreover, with the concentration. The initial differences in rotation have obviously, in this particular case, no connexion whatever with the isodynamic transformation, which is the cause of the mutarotation, and it is claimed by the author that the differences represent true solvent and concentration effects.

[60] T. S. Patterson, *T.*, 1916, **109**, 1204.

[61] H. E. Armstrong and E. E. Walker, *Proc. Roy. Soc.*, 1913, [A], **88**, 388; *A.*, 1913, ii, 543.

In so far as the variable rotations are attributed by the theory of dynamic isomerism to variations in the proportion of the α- and β-forms of nitrocamphor, the claim appears to be perfectly valid, but, to the writer, it would seem that the elasticity of the theory is such that the postulation of mutually transformable isomerides of a more refined and elusive type should present no difficulty.

The occurrence of maxima on the temperature–rotation curves of certain active substances is also said to militate strongly against the theory of isodynamic equilibrium. This argument appears to be sound, for although maxima or minima are not impossible from the point of view of the theory of dynamic isomerides, the explanation of these by a displacement of the equilibrium would involve consequences which it would be difficult to accept.

To turn to the special case of ethyl tartrate, which shows large variations in rotatory power under the influence of varying temperature, solvent, and concentration, and has been largely used by Patterson in his investigations, it has been stated [62] that this substance is a mixture which can be separated by fractional distillation into portions which differ widely in rotatory power, more particularly for violet light. There is no doubt that this statement was meant to convey the impression that pure ethyl tartrate had been separated into fractions containing varying proportions of two active forms of dissimilar constitution, but the experimental data subsequently brought forward [63] in its support cannot be regarded as affording adequate proof of the statement. Of several fractions which were obtained by Lowry and Dickson, the purest would seem to be somewhat less pure than the ester which has been used in Patterson's investigations. There is consequently no direct evidence to support the view that the variation in the rotatory power of ethyl tartrate with temperature, solvent, and concentration can be interpreted in terms of dynamic isomerides.

The absence of such direct evidence is perhaps not of essential importance, for the assumption of a sufficiently rapid adjustment of the isodynamic equilibrium avoids any difficulty which may arise in this direction. On the other hand, Patterson points out that isodynamic change in a substance like ethyl tartrate would, on grounds of analogy, be expected to take place relatively slowly.

In a further paper, in which the evaluation of dispersive power has been examined, the use of the ordinary dispersion-coefficient is adversely criticised [64] on the ground that this function is not a

[62] T. M. Lowry and T. W. Dickson, *Trans. Faraday Soc.*, 1914, **10**, 59; *A.*, 1914, ii, 786.

[63] T. M. Lowry and T. W. Dickson, *T.*, 1915, **107**, 1173; *A.*, 1915, ii, 660.

[64] T. S. Patterson, *ibid.*, 1916, **109**, 1176.

characteristic constant, but may assume values between 0 and $\pm\infty$ for comparatively slight variations in the external conditions. To overcome this difficulty it is recommended that the rotations should be measured from an arbitrary or rational zero, which depends on the nature of the active substance and on the wave-lengths of the light which is employed in the investigation of the dispersion. The rational zero is determined by the point of intersection of the temperature–rotation curves or of the straight lines corresponding with these wave-lengths on the characteristic diagram, which in itself is merely a convenient method of plotting rotation–dispersion curves. If α_v and α_r are the specific rotations for violet and red light respectively and α_0 is the rational zero as found by the above procedure, then the ordinary dispersion ratio is given by α_v/α_r, whilst the rational dispersion ratio is represented by $(\alpha_v-\alpha_0)/(\alpha_r/1-\alpha_0)$. When the rational coefficient is used as a measure of dispersive power, numbers are obtained which exhibit a degree of constancy for variations in the temperature, concentration, and nature of solvent which seem to warrant the conclusion that the dispersive power is more suitably measured in this way than by the use of the ordinary dispersion ratio.

The propriety of the usual method of comparing rotation data is also considered in a paper[65] on magnetic rotatory dispersion in relation to the electron theory. In comparing the refractive powers of different compounds, the necessity for expressing the refraction in terms of the free frequencies of the resonators has been recognised by the general adoption of the Lorenz–Lorentz formula, the use of which eliminates the polarisation effects in the immediate vicinity of the molecules and reduces the actual frequency of the electron to the value which it would have if the atom were isolated. The author contends that polarisation effects should be eliminated from the rotation data by a similar method. If this is done, the quantity in terms of which different substances are to be compared is $Rn/(n^2+2)^2$, in which R is the molecular rotation and n the refractive index of the substance for the monochromatic light used. In terms of this quantity it is shown that the magnetic molecular rotatory powers of various compounds may be calculated from constants which represent the rotational effects of various groupings, such as C–H, C–C, C–O, and C=O.

Chemical Reactivity. Catalysis.

In view of the success which has been achieved by the quantum theory in its application to the interpretation of physical pheno-

[65] S. S. Richardson, *Phil. Mag.*, 1916, [vi], **31**, 454; *A.*, ii, 280.

mena, it is not surprising that attempts should have been made to apply this theory to physico-chemical changes. The idea that ordinary or thermal reactions may be due to infra-red radiation seems to have been first suggested by Trautz,[66] and later an explanation of various physico-chemical processes in terms of infra-red radiation was put forward by Krüger.[67]

In last year's Report[68] reference was made to the further development of this idea in relation to the phenomena of catalysis and the influence of temperature on the velocity of chemical change. Since that time the infra-red radiation hypothesis has been discussed in greater detail, and an attempt made to give it a quantitative expression.[69]

To realise the nature of this development it must be remembered that the radiation hypothesis, as applied to chemical reactivity, is intimately bound up with the view that the molecules of a substance become reactive when the total energy content reaches a certain critical value, and the line of argument which leads to this view, first developed by Marcelin and stated in more precise form by Rice,[69a] is based on considerations of statistical mechanics.

The radiant energy required to raise the energy content of individual molecules to the value corresponding with the reactive condition is supplied in the form of quanta and absorbed by the reacting substance. The density of this absorbable radiation is obviously a factor which influences the rate at which the molecules become reactive, and is therefore of prime importance in relation to the velocity of reaction.

In the ordinary formulation of the law of mass action, the active mass is generally represented by the volume concentration of the reacting molecular species, and the velocity is accordingly given by the equation $v = kc_1^{n_1}c_2^{n_2}c_3^{n_3}$ . ., in which k is the so-called affinity-coefficient. According to the radiation hypothesis, k may be resolved and the density of the absorbable radiation represents one of the component factors. In the case of a unimolecular reaction, the velocity is, on this view, proportional to the product of the concentration of the reactive substance and the density of the absorbable radiation, the density representing the number of quanta present in unit volume of the system when the radiation and matter are in thermal equilibrium.

By reference to the quantum theory, it may be shown that the

[66] M. Trautz, *Zeitsch. wiss. Photochem.*, 1906, **4**, 160.

[67] F. Krüger, *Zeitsch. Elektrochem.*, 1911, **17**, 453 ; *A.*, 1911, ii, 789.

[68] See p. 20.

[69] W. C. M. Lewis, *T.*, 1916, **109**, 796 ; *A.*, ii, 559.

[69a] J. Rice, *Rep. Brit. Assoc.*, 1915, 397. Compare also *Trans. Faraday Soc.*, 1915, **11**, 1.

radiation density depends on the frequency of the radiation, the temperature, and the refractive index of the system for the frequency in question. The last-mentioned factor is of particular significance for the radiation hypothesis, for, in dealing with radiation of the absorbable type, we are concerned with radiation in the neighbourhood of an absorption band. In passing through an absorption band, the refractive index undergoes marked changes in value, and is abnormally large on the greater wave-length side. Since the radiation density varies as the cube of the refractive index, it follows that quanta corresponding with the wave-length region just below the band will be present in relatively large quantity in the system. This modification in the distribution of the infra-red radiation, which may be thus interpreted in terms of the absorption bands of one or other of the substances present, is supposed to be the cause of the effects which are usually described as solvent or catalytic effects.

Apart from solvent and catalytic influences, reactivity increases with rise of temperature, and this also is attributed to an increase in the radiation density. Expressions derived to represent the influence of temperature are shown to be in agreement with Arrhenius's empirical formula for small intervals, and lead, moreover, to the conclusion that the temperature-coefficient will be diminished in presence of a positive catalyst and increased when a negative catalyst is added. The available experimental data would seem to be in agreement with this deduction.

The idea that an increase in the velocity of reaction is accompanied by a diminution in the temperature-coefficient has been arrived at quite independently [70] by a line of theoretical reasoning which avoids resort to the usual conception of chemical equilibrium as being the result of a balance between opposed dynamic processes. The argument leads to the conclusion that the temperature-coefficient of a reaction will deviate from what is usually regarded as the normal value when the velocity of the reaction is very large or very small. In the case of excessively rapid reactions, it is to be expected that the temperature-coefficient will diminish as the velocity increases and approximate to a limiting value of unity, whilst for reactions of exceedingly small velocity the temperature-coefficient may be expected to increase rapidly as the velocity falls.

Although, in general, there would seem to be little in common between the influence of temperature on the one hand, and the influence of other variables, such as concentration, nature of the solvent, catalysts, and the action of light on the other, it is supposed that the effect produced by changes in all these variables is in much

[70] A. Skrabal, *Monatsh.*, 1916, **37**, 495; *A.*, ii, 606.

the same way dependent on the order of magnitude of the reaction velocity itself. The above relation between the velocity and the temperature-coefficient is, on this view, the special expression of a more general parameter rule, according to which, if p represents any one of the parameters on which the velocity of the reaction k depends, then increase in k will be accompanied by a diminution in the value of the parameter-coefficient, dk/dp, and the parameter quotient, $k_{p+\Delta p}/k_p$, will approximate to a limiting value of unity.

Electrical Transference in Amalgams.

The idea that metallic solutions are analogous to aqueous solutions of electrolytes has been met with the objection that transport experiments have yielded no evidence of changes in concentration on the passage of a current. Recent experiments,[71] in which a strong current was passed through sodium and potassium amalgams under conditions which eliminated as far as possible the influence of convection, have led to the somewhat remarkable conclusion that the passage of the current is accompanied by the transfer of the alkali metal from the cathode to the anode. The number of equivalents transferred per faraday is very small, and decreases with diminishing concentration of the alkali, but the authors entertain no doubt in regard to the reality of the result. The explanation offered attributes the conductivity entirely to electrons, and if this view is correct it would seem that the amalgams differ essentially from solutions of the alkali metals in liquid ammonia, which, according to Kraus, owe their conductivity to positive alkali metal ions and free electrons.

H. M. Dawson.

[71] G. N. Lewis, E. Q. Adams, and (Miss) E. H. Lamman, *J. Amer. Chem. Soc.*, 1915, **37**, 2656, ; *A.*, 1916, ii, 76.

INORGANIC CHEMISTRY.

Although the number of papers dealing with inorganic chemistry that have been published during this last year shows a marked decrease, many of them deal with subjects of great interest. Notably is this the case with the investigations of the atomic weights of the isotopes of lead and thorium. The last doubt must now be banished from the mind of the most pronounced sceptic as to the definite existence of isotopes with identical chemical properties, but with markedly different atomic weights. The discovery recorded during this year of the fact that common lead and radio-lead have the same atomic volume would seem to give the final proof.

The enunciation of this theory by Soddy and by Fajans, and its proof by Richards and by Hönigschmid, must surely rank as one of the most striking advances that has taken place in chemistry during recent years. Moreover, its intrinsic value in supporting the modern views as to the structure of atoms is obvious.

In the following Report the opportunity has been taken of including a review of the work which has been carried out during the last four years on the chemistry of the rare earths.

Atomic Weights.

The International Committee, in their report for 1916,[1] only make one change in the list of atomic weights as printed for 1915. They recommend that the value of 93·1 be adopted for the atomic weight of columbium. This change is based on work described in last year's Report.[2] From the determinations of atomic weights that have been made in the past twelve months the following may be selected.

Hydrogen.—A very accurate determination has been made of the ratio of combining volumes of hydrogen and oxygen.[3] The

[1] *T.*, 1916, **109**, 777.

[2] E. F. Smith and W. K. van Haagen, *J. Amer. Chem. Soc.*, 1915, **37**, 1783 ; *A.*, 1915, ii, 692.

[3] F. P. Burt and E. C. Edgar, *Phil. Trans.*, 1916, [A], **216**, 393 ; *A.*, ii, 427.

hydrogen was prepared by the electrolysis of a solution of barium hydroxide which had four times been recrystallised. The gas was purified either by means of cocoa-nut charcoal at the temperature of liquid air or by passage through an electrically heated palladium tube. The oxygen was prepared by the electrolysis of barium hydroxide or by heating potassium permanganate. It was purified by condensation and subsequent fractionation. The volumes of the gases were actually measured at 0° and 760 mm., in order to obviate the necessity of correction for temperature and pressure. One volume of oxygen was exploded with rather more than two volumes of hydrogen, and these volumes were measured consecutively in the same apparatus, and at the end the volume of residual hydrogen was measured In this way the formation of ozone, hydrogen peroxide, and oxides of mercury was eliminated. From five series of experiments the volume ratio was found to be 2·00288 at 0° and 760 mm. From Morley's values for the weights of 1 litre of hydrogen (0·089873) and oxygen (1·42900) this ratio gives the atomic weight of hydrogen as 1·00772. On the other hand, recent work renders probable a somewhat higher value for oxygen, 1·42905, this being the value proposed by Germann as a slightly weighted mean of his results combined with those of Rayleigh and of Morley.[4] If this figure is adopted, the atomic weight of hydrogen is found to be 1·00769, and this would seem to be the most accurate value yet obtained. It should be pointed out that a sixth series of experiments was carried out with oxygen in slight excess, and the result obtained from these shows that there is no constant error introduced by the use of the slight excess of hydrogen.

In this connexion reference may be made to the pressure exerted by the same volume of gas in vessels of different shape. Morley found the ratio of combining volumes of hydrogen and oxygen to be 1 : 2·00023, while Scott found the ratio to be 1 : 2·00285. Morley measured the gases in a eudiometer tube, whilst the latter used spherical vessels, and Morley suggested that the difference might in some way be due to the difference in shape of the measuring vessels. A careful comparison has been made of the volume occupied by a gas in a system of tubes with that which it occupies in a bulb.[5] The difference does not exceed 1 in 10,000, whilst the above ratios differ by 1 in 1000.

Bromine.—A series of determinations has been made of the density of hydrogen bromide.[6] The gas was prepared by the action

[4] A. F. O. Germann, *J. Chim. phys.*, 1914, **12**, 66 ; *A.*, 1914, ii, 454

[5] W. A. Noyes and L. C. Johnson, *J. Amer. Chem. Soc.*, 1916, **38**, 1017 ; *A.*, ii, 375.

[6] E. Moles, *Compt. rend.*, 1916, **162**, 686 ; **163**, 94 ; *A.*, ii, 314, 526.

of water on phosphorus tribromide, bromine on hydrogen sulphide, bromine on naphthalene at the ordinary temperature, and on paraffin heated at 200°. The gas was very carefully purified in each case. As a mean of thirty-three determinations the weight of 1 litre of 0° and 760 mm. was found to be 3·64442±0·00013 grams. The weight of the gas under diminished pressures was also determined and the coefficient of compressibility obtained. The molecular weight of the gas was thus found to be 80·934, whence the atomic weight of bromine is found to be 79·926 (H=1·008).

Cadmium.—In last year's Report reference was made to the value of 112·417 obtained for the atomic weight of cadmium by Baxter and Hartmann,[7] and to the criticism made by Hulett and Quinn, who obtained the figure of 112·3.[8] During this year the former authors give the results of some further measurements by the same method, namely, the electrolysis of cadmium bromide solutions with a mercury cathode. As a mean of twelve determinations, the atomic weight was found to be 112·407.[9] An analogous series of determinations with cadmium chloride gave the figure 112·413. On the other hand, a low result for the atomic weight has been published by Œchsner de Coninck and Gérard.[10] The method adopted was to dissolve the cadmium in sulphuric acid, the resulting solution being treated with hydrogen sulphide. The cadmium sulphide, after washing, was dissolved in concentrated hydrochloric acid, the excess acid evaporated, and the cadmium precipitated as carbonate by the addition of a large excess of ammonium carbonate. A weighed quantity of the pure cadmium carbonate was reduced to metal in a current of pure hydrogen. As a mean of five determinations, the atomic weight was found to be 112·32. It should be pointed out, however, that owing to the amounts employed a small error in the weighing would affect the result to an abnormally great extent, and therefore perhaps too great value should not be placed on this result.

Zinc.—By a method similar to that described under cadmium, namely, the electrolysis of a solution of the bromide, the atomic weight of zinc as a mean of eight determinations was found to be 65·388.[11] The zinc before use was very carefully purified, and

[7] G. P. Baxter and M. L. Hartmann, *J. Amer. Chem. Soc.*, 1915, **37**, 113; *A.*, 1915, **11**, 98.

[8] G. A. Hulett and E. L. Quinn, *ibid.*, 1915, **37**, 1997; *A.*, 1915, ii, 771.

[9] G. P. Baxter, M. R. Grose, and M. L. Hartmann, *ibid.*, 1916, **38**, 857; *A.*, ii, 327.

[10] W. Œchsner de Coninck and Gérard, *Compt. rend.*, 1915, **161**, 676; *A.*, ii, 33.

[11] G. P. Baxter and M. R. Grose, *J. Amer. Chem. Soc.*, 1916, **38**, 868; *A.*, ii, 327.

a spectroscopic test showed the presence of only minute traces of cadmium, estimated at 0·001 per cent.

Uranium.—The previous determinations of the atomic weight of this element have been made with material prepared from pitchblende. It has been thought worth while to repeat the determinations with uranium obtained from another source, and the crystallised uranium ore from Morogoro, referred to in last year's Report, was used. The Pb : U ratio would lead to the conclusion that this ore is eight hundred million years old as against two hundred and fifty million years for pitchblende. This Morogoro ore is almost free from impurities. The values obtained from two series of determinations were 238·043±0·018 and 238·159±0·023,[12] the method being the determination of the ratio UBr_4 : AgBr, as previously described. The value obtained in the second series is very close to the old value of 238·175,[13] which led the International Committee to adopt the figure 238·2.

A very interesting series of papers has appeared on the atomic weights of the isotopes of thorium and lead, which may be described in some detail. The case of thorium and its isotope ionium may first be dealt with.

Measurements have been made of the atomic weight of thorium obtained both from minerals rich in uranium and from minerals poor in uranium.[14] The former specimens of thorium are rich in ionium. Now thorium and ionium are isotopes and identical in their chemical and physical properties, but they should have different atomic weights. The method employed was to obtain the ratios $ThBr_4$: 4Ag and $ThBr_4$: 4AgBr, the purification of the material being similar to that adopted for uranium bromide, and already described. The values obtained for the atomic weight were as follows:

$ThBr_4$: 4Ag, 232·152.
$ThBr_4$: 4AgBr, 232·150.
(Th·Io)Br_4 : 4Ag, 231·507.
(Th·Io)Br_4 : 4AgBr, 231·502.

It is clear from these figures that ionium has a lower atomic weight than thorium. The mean value for the atomic weight of thorium, 232·151±0·0165, is considerably lower than the international value of 232·4, but it is believed to be more correct. The difference between the two values is discussed at some length in a

[12] O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1916, **37**, 185; *A.*, ii, 484.

[13] O. Hönigschmid, *Zeitsch. Elektrochem.*, 1914, **20**, 452; *Compt. rend.*, 1914, **158**, 2004; *A.*, 1914, ii, 662.

[14] *Ibid.*, 1916, **22**, 18; *A.*, ii, 407.

later paper.[15] The international value depends on the conversion of anhydrous thorium sulphate into the oxide, and this method is adversely criticised. The determinations with thorium bromide were repeated with material from repeatedly recrystallised thorium ammonium nitrate and with a preparation purified by the sulphate method, followed by the iodate method. Both gave identical results. Two independent series, one of twelve and the other of fifteen experiments, gave $232{\cdot}15 \pm 0{\cdot}016$ and $232{\cdot}12 \pm 0{\cdot}014$, the latter value being the more probable. As regards the atomic weight of ionium, the question is discussed in a third paper. The atomic weight should be either $238{\cdot}18 - 8 = 230{\cdot}18$ if calculated from uranium, or $226{\cdot}0 + 4 = 230{\cdot}0$ if calculated from radium. The atomic weight was again determined with an ionium preparation made by Auer von Welsbach, which was spectroscopically identical with the thorium used in the previous work. The atomic weight of this material was found to be $231{\cdot}51 \pm 0{\cdot}014$.[16] If 230 were the true atomic weight of ionium, this would mean 30 per cent. of ionium and 70 per cent. of thorium in the preparation.

Lead.—A further investigation has been made of the atomic weight of lead from radioactive minerals.[17] Four samples of radio-lead were obtained from widely differing sources, namely, Australian carnotite, American carnotite, Norwegian cleveite, and Norwegian bröggerite. Two investigations were made with common lead from galena as a control, and the values obtained for the atomic weight were 207·179 and 207·188, giving a mean of 207·183. The results obtained with the four samples of radio-lead may be tabulated as follows:

Australian carnotite (four analyses), 206·342.
American carnotite (two analyses), 207·004.
Norwegian bröggerite (one analysis), 206·122.
Norwegian cleveite (two analyses), 206·084.

The value obtained for the lead from cleveite is essentially the same as that obtained by Hönigschmid and Horovitz[18] with radio-lead from bröggerite, namely, 206·06, whilst the Norwegian bröggerite has given a value so near that it may be presumed that the lead is of the same type. The two carnotites, on the other hand, give widely differing results. The Australian carnotite certainly contained galena, and therefore the radio-lead may have been mixed

[15] Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1916, **37**, 305; *A.*, ii, 510.

[16] *Ibid.*, 335; *A.*, ii, 510.

[17] T. W. Richards and C. Wadsworth 3rd, *J. Amer. Chem. Soc.*, 1916, **38**, 2613.

[18] O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1915, **36**, 355; *A.*, 1915, ii, 635.

with common lead. The value of 206·34 would be given by a mixture of one part of common lead with three parts of radio-lead, such as is obtained from the cleveite. On the other hand, the American carnotite is very puzzling, since the value obtained would point to a mixture of one part of radio-lead with five or six parts of common lead. This would mean a very large amount of galena in the carnotite. Some uncertainty about the source renders it impossible to say whether this explanation is satisfactory. Alternatively, it might be assumed that there is a third variety of radio-lead, with yet higher atomic weight, such as that indicated by Soddy and Hyman.[19] Measurements were made of the radioactivity of the four samples of radio-lead in the form of chloride, and it was found that the radioactivity of the lead from the American carnotite was the greatest and that from the Australian carnotite the least. The radioactivity cannot, therefore, be due to the isotope of lowest atomic weight. It is more probably due to radium-*E*. Very careful investigation showed that there is no difference whatever in the spark spectra of ordinary and radio-lead.

Concurrently with the atomic weight determinations of radio-lead, measurements have been made of its density.[20] It is found that the density of radio-lead from Australian carnotite as determined by the pyknometer method at 19·94° is 11·288, whilst that of ordinary lead is 11·337. The density of the radio-lead from cleveite is 11·273. From the values of the atomic weights given above, the atomic volumes of common lead and the radio-leads from carnotite and cleveite are 18·277, 18·279, and 18·281 respectively. In other words, the atomic volumes of lead and its isotope are identical. This fact is highly significant in view of the disintegration theory put forward by Soddy and by Fajans.

A very important series of papers has been published on the errors which affect atomic weight determinations.[21, 22, 23, 24] In the first of these the various errors are discussed which are involved in weighing and the reduction of the weights to a vacuum. It is shown that there are ten sources of error, and the probable values of these are given. If these errors are not eliminated, an error of 0·19 mg. is possible in any given determination. It is pointed out

[19] F. Soddy and H. Hyman, *T.*, 1914, **105**, 1402.

[20] T. W. Richards and C. Wadsworth 3rd, *J. Amer. Chem. Soc.*, 1916, **38**, 221, 1658; *A.*, ii, 251, 566.

[21] P. A. Guye, *J. Chim. phys.*, 1916, **14**, 25; *A.*, ii, 385.

[22] T. Rénard and P. A. Guye, *ibid.*, 1916, **14**, 55; *A.*, ii, 386.

[23] P. A. Guye, *ibid.*, 1916, **14**, 83; *A.*, ii, 386.

[24] P. A. Guye and F. E. E. Germann, *ibid.*, 1916, **14**, 195, 204; *A.*, ii, 445, 432.

that values of atomic weights purporting to be accurate to 1 part in 500,000 are somewhat illusory.

It is further pointed out that recent determinations of the atomic weight of silver are not sufficiently concordant, and it is suggested that this is partly due to the presence of gaseous impurities in the metal. Experiment shows that after bubbling hydrogen through molten silver, certain gases, notably carbon monoxide, are retained in sufficient amount to account for appreciable variations in experimentally determined atomic weights. Further, the gas content of the silver varies throughout the cooled mass. Considerable interest attaches to the question of purity of substances, and the classic work of de Gramont on the ultimate spectrum lines has enabled the use of the spectroscope as a means of detecting impurities, since it is now known which spectrum lines show themselves when impurity is present in very small amounts. de Gramont gives the impurities which are present in forty-two solid elements, dividing them into two classes, namely, those which are generally present and those which are always present whether the element is free or in the form of a simple salt, however rigid the purification has been.[25] He directs special attention to the case of silver, which always contains traces of calcium, copper, gold, and magnesium, and he points out the great importance of this in reference to the use of the atomic weight of silver as a standard in other determinations of atomic weight.

Molecular Weights.

In this section only one paper of importance has appeared during the year, and in this is described the determination of the molecular weights of certain substances in bromine solution.[26] The method adopted was to aspirate air through the solution at a known temperature and to estimate the bromine carried off by a given volume of air by means of a solution of potassium iodide. The molecular weights were calculated from the formula $M = P'Sm/(P-P')s$, where M and m are the molecular weights of the solvent and solute, S and s their weights in grams, P the vapour pressure of the pure solvent, and P' that of the solution. Antimony bromide, stannic bromide, and iodine monobromide were found to be unimolecular, whilst a solution of sulphur consisted of diatomic molecules.

[25] A. de Gramont, *J. Chim. phys.*, 1916, **14**, 336; *A.* ii, 589.
[26] R. Wright, *T.*, 1916, **109**, 1134.

Specific Heats.

Reference was made in last year's Report to the determination of the specific heat of copper at 15·2° and 21·5° abs.[27] These measurements have now been repeated with a considerably improved apparatus,[28] and the following values for the atomic heat of copper were obtained:

Atomic heat.	T. abs.
0·0396	14·51°
0·1155	20·19
0·234	25·37
0·870	40·22

If these values be compared with those calculated from the equation $C = kT^3$, it will be found that the atomic heat decreases with falling temperature more rapidly than it should do according to Debye's law. The atomic heat of solid nitrogen has also been determined, and it is found to increase from 1·60 at 15·27° abs. to 5·48 at 61·68° abs. The variation of the atomic heat with temperature differs considerably from that found with monatomic solids, and therefore the conclusion is drawn that crystallised nitrogen consists of diatomic molecules.[29]

The ratio of the two specific heats for various gases has been determined by Kundt's method with tubes of different diameters and notes of different pitch.[30] The results obtained would seem to show that the molecular heats increase with the density of the gas. Thus, the following values were obtained for the molecular heats at constant pressure: carbon monoxide, 6·900; nitrogen, 6·905; oxygen, 6·924; hydrogen chloride, 7·046; carbon chloride, 8·904; water vapour, 9·214; sulphur dioxide, 10·059; ammonia, 8·933; ethylene, 9·773; acetylene, 9·783.

Allotropy.

The conclusions drawn by Cohen and Helderman[31] as to the existence of two enantiotropic modifications of copper with a transition temperature of 71·7° have been adversely criticised.[32] Com-

[27] W. H. Keesom and H. K. Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 894; *A.*, 1915, ii, 83.

[28] *Ibid.*, 1915, **18**, 484; *A.*, ii, 12.

[29] *Ibid.*, 1916, **18**, 1247; *A.*, ii, 371.

[30] G. Schweikert, *Ann. Physik*, 1915, [iv], **48**, 593; 1916, [iv], **49**, 433; *A*, ii, 79, 216.

[31] E. Cohen and W. D. Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 628; *A.*, 1914, ii, 205. *Ibid.* 1914, **17**, 60; *A.*, 1914, ii, 654.

[32] G. K. Burgess and J. N. Kellberg, *J. Washington Acad. Sci.*, 1916, **5**, 657; *A.*, ii, 102.

parative measurements have been made with copper and platinum wire resistance thermometers wound on the same frame, and it is found that platinum shows similar changes in conductivity to those of copper when exposed alternately to temperatures of 0° and 100°. Both metals, however, give constant results after a few alternations. A detailed study was made of the resistance of copper over the range of 0° to 100°, but only negative results were obtained, and it is concluded that there is no evidence for the existence of a metastable modification of copper. It must, however, be remembered that Cohen and Helderman based their conclusions as to the allotropy of copper upon dilatometric measurements, and they only mentioned as collateral evidence the variations in electrical resistance of copper noted by Matthiessen and Bose after the copper had been kept some days at a temperature of 100°.[33]

Reference was made in the Report of 1914 to the new black allotropic modification of phosphorus[34] prepared by heating ordinary yellow phosphorus at 200° at 12,000 kilograms/cm.^{2} Some further very interesting work on the allotropy of phosphorus may be recorded. There is no doubt that black phosphorus is a definite allotropic modification and that red phosphorus is not a definite substance, for it varies greatly in appearance and density according to the method of preparation.[35] The varieties close to the upper limits of density are violet in appearance, and have been named by Smits violet phosphorus. This modification may be prepared as follows. Ordinary white phosphorus with a trace of sodium as catalyst is subjected to a pressure of 4000 kilograms/cm.^{2} at the ordinary temperature, and then heated at constant volume to 200°. The rise of pressure was only 500 kilograms. At 200° the pressure was raised to 12,500 kilograms for twenty minutes, and then to 130,000 kilograms for forty-five minutes. No black phosphorus was formed. The apparatus was cooled, and the pressure released at the ordinary temperature. The white phosphorus was entirely transformed into violet phosphorus, but a small piece of bright red phosphorus which had been placed under the white was unchanged. The density of the violet phosphorus prepared in this way was 2·348. A piece of violet phosphorus, together with a small quantity of bright red phosphorus, was subjected to pressure and heat in the presence of iodine as catalyst. None of the black modification was formed, but the red phosphorus was

[33] Matthiessen and Bose, *Ann. Phys. Chem.*, 1862, **115**, 353.

[34] P. W. Bridgman, *J. Amer. Chem. Soc.*, 1914, **36**, 1344; *A.*, 1914, ii, 647.

[35] *Ibid.*, 1916, **38**, 609; *A.*, ii, 246.

converted into the violet modification. Evidently, therefore, the violet modification is the stable form as compared with the red modification at 200° between 8000 and 12,000 kilograms/cm.^{2} It was not found possible to convert red phosphorus into black phosphorus, as a mixture of red and white phosphorus simply changed into a mixture of red and black phosphorus when heated at 200° and 12,500 kilograms/cm.^{2}

An interesting observation was made on the rate of change of white phosphorus to black phosphorus. After the pressure is raised to 12,000 kilograms at 200°, the black modification is never produced instantaneously. There always is shown a period of preparation lasting from ten to thirty minutes, during which period the pressure decreases slowly. The rate of decrease increases gradually until a critical point is reached, when a sudden transformation of the entire mass to the black modification takes place. In one experiment, the total drop of pressure during the preliminary stage was 400 kilograms in fifteen minutes, and during the transition the pressure dropped more than 8000 kilograms. It is thus proved that the black modification is stable compared with white phosphorus at 200° and pressures above 4000 kilograms. The violet modification is stable compared with the white modification at 4000 kilograms and temperature somewhat below 200°. The violet modification is stable compared with red phosphorus at 200° between 8000 and 12,000 kilograms.

Some attempts have been made to compare the vapour pressures of black and violet phosphorus,[36] but the results obtained were unsatisfactory, owing to the difficulty of removing the kerosene from the former, the kerosene having been used as pressure-liquid in its preparation. At temperatures below 550°, the vapour pressure of black phosphorus did not reach a constant value. At somewhat higher temperatures a constant value was reached, which is nearly equal to that of violet phosphorus. At 570° the black modification has a higher vapour pressure than the violet modification. In the presence of iodine as catalyst, the melting points of black and violet phosphorus were found to be 587·5° and 589·5° respectively.

Smits's theory of allotropy has been applied with some success to phosphorus.[37] When violet phosphorus is rapidly and partly vaporised in a vacuum at a temperature at which internal equilibrium is only slowly set up, a substance of abnormally low

[36] A. Smits, G. Meyer, and R. P. Beck, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 992; *A.*, ii, 185.

[37] A. Smits and S. C. Bokhorst, *Zeitsch. physikal. Chem.*, 1916, **91**, 249; *A.*, ii, 317.

vapour pressure is obtained. The more volatile component has been expelled at a temperature at which it can only slowly be re-formed. The vapour pressure of this component increases continuously at constant temperature, and, after the addition of 0·1 per cent. of iodine and heating at 410°, the internal equilibrium is again set up and the vapour pressure becomes normal. This explains the use of iodine in the melting-point determinations mentioned above. It is concluded that red phosphorus is not an homogeneous substance, and the name "red-coloured phosphorus" is suggested.

Colloids.

An ingenious method has been tried with the view of determining the relative quantities of free, capillary, and combined water in inorganic gels.[38] Since the total water content is known, it then becomes possible to calculate the composition of the gel. The principle of the method is a progressive freezing of the water, when the free and capillary water solidifies at different temperatures. A weighed quantity of the hydrogel is placed under light petroleum in a dilatometer, and the whole is slowly cooled. The dilatometer readings at first show a regular decrease, due to the contraction of the bulb and its contents. At a temperature usually several degrees below 0°, a sudden expansion occurs due to freezing. The water which freezes during this expansion consists of free water and that part of the capillary water the freezing point of which has been reached. After the volume has become constant, a further lowering of the temperature causes more capillary water to freeze, and the volume usually expands a little more. After this the volume begins to contract, and after the temperature has been sufficiently lowered the contraction becomes a linear function of the temperature. On raising the temperature again, the expansion is nearly linear for some distance, but at a temperature below 0° contraction sets in, due to the melting, and the volume finally returns to its original value above 0°. It was not found possible sharply to distinguish between true capillary and free water, for the reason that supercooling always occurs. Determinations, however, could be made of the amount of capillary water freezing below a certain temperature, and the temperature chosen was −6°. The true capillary water is therefore rather greater in amount than this apparent capillary water.

A number of preliminary experiments were tried with moist sand and moist lampblack in order to test the method and to observe the difference between free and capillary water. Sand

[38] H. W. Foote and B. Saxton, *J. Amer. Chem. Soc.*, 1916, **38**, 588; *A.*, ii, 230.

and water gave an example of a mixture containing only free water. In this case, freezing occurred at $-4°$, and the whole of the expansion took place at this temperature, the contraction above and below $-4°$ being perfectly regular. The amount of water present in the quantity of sand taken was 1·404 grams, and the amount estimated from the expansion was 1·430 grams.

A sample of lampblack, which had previously been well ignited, was moistened with water and allowed to remain a few days. Although nearly dry to the touch, it then contained more than 40 per cent. of water. The first expansion took place at $-6°$, but the whole of the water was not frozen until the temperature had remained at $-28°$ for two hours. The total quantity of water in the sample taken was 1·834 grams and the total estimated was 1·831 grams, and of this 1·207 grams was apparently capillary water.

Experiments were made with the gels of alumina, silica, and ferric oxide, and also on the effect of ageing the gels by repeated freezing and remelting. The effect on the alumina gel is to cause the capillary water to become free, whilst the silica gel reabsorbs the capillary water after it has been frozen and remelted. One case of an alumina gel containing 51·90 per cent. of water was found to have 37·1 per cent. in the combined state, the percentage in $Al(OH)_3$ being 34·6. Two gels of silica possessed combined water corresponding with the formulæ $SiO_2,1·31H_2O$ and $SiO_2,1·35H_2O$, whilst a gel of ferric oxide contained combined water agreeing with the formula $Fe_2O_3,4·25H_2O$.

The interesting case of the doubly refractive sol of vanadium pentoxide has been studied somewhat extensively.[39, 40] If a concentrated solution of the sol is made to flow through a tube of triangular cross-section, which is used as a prism, it is found that the hydrogen red spectrum line is resolved into two oppositely polarised lines. The more strongly refractive ray has its vibrations parallel to the direction of flow, and therefore parallel to the major axes of the colloidal particles. When the solution is stirred, it exhibits yellow, shining streaks, and if a similar solution is examined by transmitted light, it is seen to be quite clear, and dark streaks are observed. The same phenomena can be seen if, instead of stirring, the sol is placed in a magnetic or electric field. When the sol is examined by the ultramicroscope,[41] the presence is seen

[39] H. Diesselhorst and H. Freundlich, *Physikal. Zeitsch.*, 1915, **16**, 419; *A.*, ii, 65.

[40] H. Freundlich, *Zeitsch. Elektrochem.*, 1916, **22**, 27; *A.*, ii, 442.

[41] H. R. Kruyt, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1625; *A.*, ii, 486.

of very elongated, rod-like structures in quiet Brownian motion, together with small round disks in a state of rapid movement. When the sol is placed in an electric field and the force lines are parallel to the direction of the luminous beam, very little dispersion takes place, and the elongated particles apparently disappear. On the other hand, when the field is perpendicular to the luminous beam, the Tyndall effect is very pronounced. All the observations are in agreement with the view that the sol is very similar to a liquid crystal.

Many substances which act as protective colloids towards the hydrosols of silver, platinum, palladium, and similar metals are ineffective in the case of colloidal mercury, for, owing to changes which take place on keeping, the mercury soon becomes insoluble. Albumins and their products of decompositions may, however, be used as protective colloids for the hydrosol of mercury,[42] and stable, therapeutically active sols of mercury can then be prepared. If a solution of mercuric chloride be added to a solution of pyrogallol, catechol, or certain aminophenols containing dextrin or glutin, a yellowish-white precipitate is obtained. On the addition of alkali, reduction takes place and colloidal mercury is formed. In this way, solid hydrosols have been prepared containing up to 80 per cent. of mercury.

If a mercuric salt is added to a solution of alkali containing dextrin or glutin, colloidal mercuric oxide is produced, and by the reaction between colloidal mercury and colloidal mercuric oxide stable preparations of colloidal mercurous oxide may be obtained.

Rare Earths.

Since the Report for 1912, no reference has been made to any work on the rare earths. It was thought preferable to leave this branch of inorganic chemistry until the occasion offered of writing a short account of the work carried out during a period of several years. There is no doubt that the annual mention of papers on this subject is unsatisfactory, because the lack of continuity thereby shown makes itself felt in this branch perhaps more than in any other.

During the interval of four years, a very considerable number of investigations have been carried out on the rare earths, many of which possess great interest. It is true that no startling discoveries have been made, and the majority of the papers that come under review deal with technique, that is to say, the methods of separating these elements the one from the other. Our knowledge of the salts of the rare earths, their properties and solubili-

[42] C. Amberger, *Kolloid Zeitsch.*, 1916, **18**, 97; *A.*, ii, 380.

ties, has greatly been enhanced. It is only right to say that this advance is due in the main to the work of Professor C. James and his co-workers. So much is this the case that it is convenient for the sake of greater continuity to discuss his papers separately.

In the following review, the first three investigations described deal with the general properties of compounds of the rare earths, whilst the later papers describe work that has been carried out on the solubilities of their many salts and the methods that have been experimented with for the purpose of effecting the separation of the rare earths from one another.

When the sulphates of the rare earths are heated, they lose SO_3 and are converted into basic sulphates, which are insoluble in water. The dissociation pressures of some of the sulphates have been measured at temperatures between 800° and 1200° with the view of obtaining a measure of their basic affinity.[43] In the following table are given the values of the dissociation pressure (P) of the sulphates in mm. of mercury at 900°, and also the heats of dissociation (Q) calculated according to Nernst's theory:

	Sc.	Sa.	Gd.	Nd.	Pr.	Er.	Yb.	Lu.	Yt.	La.
P	11·0	8·0	7·0	6·0	5·5	5·0	4·0	3·5	3·0	2·0
Q	54·5	56·6	56·9	57·2	57·4	57·6	58·2	58·5	58·9	59·8

It is evident from the above figures that the rare earths belong to the strongest bases. It is unfortunate that the dissociation pressure curves run almost parallel and very close to one another, so that it would, in general, be very difficult to separate any two rare earth sulphates by heating them to a constant, intermediate temperature, at which one gives the basic sulphate and the other remains undecomposed and soluble in water.

The ethyl sulphates[44] have been prepared of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, thulium, erbium, and neoytterbium. These salts have the general formula $M_2(EtSO_4)_6,18H_2O$, and they are strictly isomorphous, crystallising in the hexagonal system. Although the corresponding salts of scandium and indium were obtained in very small crystals, yet it was possible to conclude that they have not the same form, being monoclinic. Glucinum ethyl sulphate stands in quite a different class from the other salts, for it is a basic salt with the formula $GlO,Gl(EtSO_4)_2,4H_2O$.

The acetonylacetates of scandium, indium, and iron are isomorphous, and they form large, flat crystals quite different from the fine needles in which the corresponding salts of the rare earths

[43] L. Wöhler and M. Grünzweig, *Ber.*, 1913, **46**, 1726; *A.*, 1913, ii, 597.

[44] F. M. Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095; *A.*, 1914, i, 797.

separate out. Glucinum acetonylacetate is again quite different from all the other salts.

In the literature dealing with neodymium sesquioxide, various colours have been attributed to it, such, for example, as blue, ash-grey, green, pale violet, lavender. An investigation has shown that these contradictory statements are due to the fact that there exist hydrated oxides with different colours.[45] When neodymium hydroxide is heated at 320°, the hydrated oxide, $2Nd_2O_3,3H_2O$, is formed. This hydrate is stable up to about 500°, and has a pale brown colour tinged with rose. It heated at about 550°, it is converted into the hydrated oxide, Nd_2O_3,H_2O, the colour of which is less pronounced. Neodymium sesquioxide is only formed quantitatively at 1000°, and is blue. The various colours described by previous investigators are evidently due to their having obtained indefinite mixtures of the sesquioxide and the two hydrated oxides.

An interesting account has been published of the fractionation of the rare earths of the ytterbium group with the view of establishing once and for all the homogeneity of the element neoytterbium.[46] The method adopted was the fractional crystallisation of the nitrates, the operation being followed by measuring the coefficients of magnetisation of each fraction. After 4000 fractionations, 8 successive fractions were obtained, each having the same coefficient. This established quite definitely the elementary character of neoytterbium. As previously reported, the atomic weight was found to be 173·54. The arc spectra were measured of the two extreme fractions of the series of 8, and were found to be identical, except for a few lines in the one due to thulium and a few in the other due to lutecium. None of the rays attributed to aldebaranium[47] was seen; indeed, considerable doubt has been thrown on the existence of this as a definite element.

The glycollates of certain of the rare earths have been prepared and their properties described.[48] The glycollates of the earths of the cerium group are anhydrous and crystallise in crusts, whilst those of the earths of the yttrium group crystallise in needles, with two molecules of water of crystallisation. The yttrium salt is the least soluble, then follow the lanthanum, cerium, and praseodymium salts, which are almost equal, and then, in order, the

[45] C. Garnier, *Arch. Sci. phys. nat.*, 1915, [vi], **40**, 93, 199; *A.*, 1915, ii, 775.

[46] J. Blumenfeld and G. Urbain, *Compt. rend.*, 1914, **159**, 323, 401; *A.*, 1914, ii, 731, 694.

[47] C. A. von. Welsbach, *Monatsh.*, 1908, **29**, 181; *A.*, 1908, ii, 591.

[48] G. Jantsch and A. Grünkraut, *Zeitsch. anorg. Chem.*, 1913, **79**, 305; *A.*, 1913, i, 247.

neodymium, samarium, and gadolinium salts. Measurements of the electrical conductivity of the solutions show, however, that complex salts are present. When lanthanum hydroxide is warmed with a solution of glycollic acid, it dissolves to form a clear solution, but at a definite temperature, which depends only on the concentration, a complex salt separates out as a precipitate. The praseodymium, neodymium, and samarium salts behave in a similar way. On the other hand, gadolinium gycollate,

$$Gd(C_2H_3O_3)_3,2H_2O,$$

crystallises without forming an unstable solution, but the yttrium salt behaves like the above.

A trial was made of using these gycollates as a means of fractionating the rare earths from xenotime, after they had been freed from cerium. Successive fractions showed a progressive increase in atomic weight, and the spectroscope revealed a concentration of neodymium and praseodymium in the last fractions.

When neutral solutions of the nitrates of the rare earths are electrolysed with a mercury cathode and platinum anode, the hydroxides are precipitated, the velocity of precipitation depending on the basicity of the rare earths.[49] Some experiments were made in order to test whether this method would be effective in separating the rare earths from one another. When a neutral solution of the nitrates of neodymium, praseodymium, lanthanum, and samarium is electrolysed, the lanthanum collects in the last fractions, and can thus be separated from the other earths of the didymium group.

Experiments have also been made on the fractional electrolysis of the rare earths from xenotime, and it was found that erbium collects in the early fractions and yttrium in the later fractions. The general results of the investigations indicate that the separation of some of the rare earths can be effected by this method more rapidly and conveniently than by the usual methods of fractional crystallisation and precipitation. It was thought possible that the precipitation of the hydroxides might be due to the production of ammonia by reduction of the nitric acid. In order to test this point, similar experiments were carried out with the chlorides of the rare earths, and analogous results were obtained, but the rate of precipitation was found to be much slower than that observed in the case of the nitrates. The nitrate experiments were repeated, using a diaphragm, and in one case, with a solution rich in erbium, holmium, thulium, and yttrium,

[49] L. M. Dennis and B. J. Lemon, *J. Amer. Chem. Soc.*, 1915, **37**, 131, 1963; *A.*, ii, 99, 775.

the first three elements were not appreciably separated from one another, but they were rapidly separated from the yttrium.

The method of fractional crystallisation of their picrates as a means of separating the rare earths from one another was first tried in 1912.[50] This method has now been studied anew.[51] A mixture of the picrates of the rare earths of the didymium group, containing small quantities of those of the yttrium and erbium groups, was submitted to 42 series of fractional crystallisations. It was found that praseodymium and neodymium tend to concentrate in the least soluble fractions, that yttrium concentrates in the most soluble fractions, whilst the metals of the erbium group are found in the intermediate fractions. In general, this method does not effect a separation of neodymium from praseodymium, but it is useful for removing small quantities of the earths of the erbium and yttrium groups from those of the didymium group, and also for the separation of yttrium from erbium and holmium.

Finally, in concluding this section of this review, a short reference may be made to a paper describing the separation from one another of the rare earths from gadolinite and xenotime.[52] Various methods of fractionation were employed. The fractions obtained by the bromate method were submitted to further fractionation by the chromate method. In this way, small quantities of yttria can rapidly be prepared from mixtures containing small amounts of erbium and holmium, but the method cannot be applied to the fractionation of mixtures which contain didymium and gadolinium unless these earths are first removed by means of potassium sulphate.

A rapid survey may now be given of the work of James and his co-workers, and in the first place brief mention may be made of the fractionation of the rare earths derived from the Carolina monazite sands. The bromate method of fractionation was used.[53] The sands contain lanthanum, cerium, praseodymium, neodymium, together with considerable quantities of samarium, gadolinium, yttrium, small amounts of dysprosium, holmium,, erbium, and minute amounts of europium, terbium, thulium, ytterbium, etc. It is not possible to give a detailed account of the work, but this brief mention will show the complexity of the problem.

An important point is raised with regard to the estimation of the rare earths, for it is found that, when they are precipitated

[50] L. M. Dennis and C. W. Bennett, *J. Amer. Chem. Soc.*,1912, **34**, 7 ; *A.*, 1912, ii, 257.

[51] L. M. Dennis and F. H. Rhodes, *ibid.*, 1915, **37**, 807 ; *A.*, 1915, ii, 347.

[52] J. E. Egan and C. W. Balke, *ibid.*, 1913, **35**, 365 ; *A.*, 1913, ii, 508.

[53] C. James, *ibid.*, 1913, **35**, 235 ; *A.*, 1913, ii, 323.

as hydroxides and ignited to the oxides, the results obtained are higher than when they are precipitated as oxalates and ignited. The explanation of this is to be found in the fact that the hydroxides tend always to carry down some of the alkali when they are precipitated, and especially is this the case when sodium hydroxide is used as precipitant.[54]

In previous papers it had been shown that yttrium can be separated quantitatively from the alkali metals by precipitation with ammonium sebacate. It is now found that lanthanum and cerium can also be separated in the same way.[55]

Sodium cacodylate as precipitant has also been experimented with as a method of separation of the rare earths. On fractionally precipitating a solution containing chiefly the chlorides of yttrium, dysprosium, and holmium with sodium cacodylate, the yttrium tends to accumulate in the early fractions, and the holmium and dysprosium in the later fractions. On boiling a mixture of the hydroxides of neodymium, samarium, and gadolinium with cacodylic acid, and fractionally crystallising the cacodylates from hot water, neodymium collects in the more soluble fractions, whilst nearly all the terbium and dysprosium remain in the least soluble portions. In this paper are described the methods of preparation and the properties of the sebacates and cacodylates of a number of the rare earths.

In the separation of the earths of the cerium and yttrium groups, the use of sodium sulphate has led to varying results. This uncertainty has been investigated, and it is found that the efficiency of sodium sulphate depends on its concentration.[56] If the solution is too concentrated, much of the yttrium earths is also precipitated.

As regards the quantitative separation of neodymium from glucinum, titanium, barium, and uranium, it is found that this can be effected by the precipitation of the neodymium as oxalate from the boiling solution.[57] Oxalic acid is used, and, after precipitation, the solution is digested until the precipitate becomes granular, when it may easily be filtered.

The preparation of the dimethyl phosphates of a number of the rare earths are described in another paper.[58] The solubilities of these salts have been determined, and it was found that they are more soluble in cold water than in hot. A trial was made of the

[54] T. O. Smith and C. James, *J. Amer. Chem. Soc.*, 1914, **36**, 909; *A.*, 1914, ii, 492.

[55] C. F. Whittemore and C. James, *ibid.*, 1913, **35**, 127; *A.*, 1913, i, 248.

[56] C. James and H. C. Holden, *ibid.*, 559; *A.*, 1913, ii, 508.

[57] T. O. Smith and C. James, *ibid.*, 563; *A.*, 1913, ii, 531.

[58] J. C. Morgan and C. James, *ibid.*, 1914, **36**, 10; *A.*, 1914, i, 135.

possibilities of this method for the separation of the rare earths. Fractionation experiments were made by preparing a solution of the rare earths in dimethylphosphoric acid. The temperature of the solution is gradually raised, and the precipitates formed are collected at definite temperatures. By the evaporation of the mother liquor additional fractions are obtained. It was found that the rate of separation of the rare earths by this method is much greater than by other methods. Lanthanum, cerium, praseodymium, and neodymium are left in the mother liquor. Samarium, europium, and gadolinium are much less soluble than these, but they are more soluble than terbium, dysprosium, and holmium. As a result of this fractionation, erbium, thulium, yttrium, and ytterbium collect in the least soluble fractions. It must be pointed out, however, that the rare earth dimethyl phosphates are inclined to decompose, with the formation of gelatinous precipitates, which render the filtration somewhat difficult.

A great number of investigations have been made in order to find the best method for the separation of yttrium from the yttrium earths. The following methods were tried: the fractional precipitation of the phosphates, monomethyl phosphates, dimethyl phosphates, cacodylates, arsenates, phosphites, chromates, bromates, and iodates, and also the fractional precipitation by means of hypophosphorus acid.[59] It was found that the chromate and phosphate methods gave the greatest efficiency. It would seem, however, that the best method is to use sodium nitrite. The rare earth oxides are dissolved in nitric acid, and the solution is diluted and boiled. A quantity of sodium nitrite is then added, which is sufficient to precipitate the required fraction of the rare earth material. The yttrium concentrates in the later fractions. This method gives a larger yield and is less expensive than either the phosphate or the chromate method. It is not very effective, however, for the separation of yttrium from terbium.

In addition to the above, various other methods for separation by fractional precipitation were tried.[60] It appears that potassium cobalticyanide is one of the most promising reagents. The rare earth cobalticyanides separate out in crystals, which have the general formula $M_2(CoC_6N_6)_2,9H_2O$.[61] Measurements were made of the solubilities of these compounds in 10 per cent. hydrochloric acid (D^{15} 1·050), and the following results were obtained, expressed in parts of the salt contained in 1000 parts of the saturated solu-

[59] H. C. Holden and C. James, *J. Amer. Chem. Soc.*, 1914, **36**, 634, 1418; *A.*, 1914, ii, 370, 657.

[60] J. P. Bonardi and C. James, *ibid.*, 1915, **37**, 2642; *A.*, ii, 102.

[61] C. James and P. S. Willand, *ibid.*, 1916, **38**, 1497; *A.*, i, 638.

tion: lanthanum, 10·41; cerium, 10·75; neodymium, 4·19; gadolinium, 1·86; yttrium, 2·78; ytterbium, 0·38. Fractional crystallisation experiments showed that a rapid separation may be obtained by the cobalticyanide method, and its use is particularly recommended for the separation of yttrium from erbium. On the large scale, fractional precipitation by means of sodium nitrite is recommended, on account of the cheapness and the ease of manipulation.

Owing to the fact that some doubt had been thrown on the homogeneity of terbium as an element, a long series of fractionations was undertaken in order, if possible, to decide the question.[62] The material employed consisted of gadolinium oxide containing terbium oxide, together with dysprosium and neodymium oxides and traces of the oxides of yttrium and erbium. From this mixture the bromates were prepared, and these were submitted to a long and careful fractionation. The results obtained leave no doubt that terbium is a single, homogeneous element. The bromate process was found to effect a comparatively rapid separation of terbium from gadolinium, and neodymium, if present, comes between these two.

Finally, reference may be made to a paper in which a very complete account is given of the separation of the rare earths, in which many of the above methods are employed.[63] The value of this paper lies in the fact that examples are given of the application of the methods to actual practice. The source of the rare earths was Brazilian monazite sand, and the material used was the solution obtained after potassium sulphate had been added to the mixed rare earth sulphates in quantity insufficient to precipitate completely the whole of the cerium metals. The solution contained considerable quantities of lanthanum, cerium, praseodymium, neodymium, in addition to samarium, gadolinium, and the earths of the yttrium group. Reference is made to the difficulty of isolating holmium, and it is said that this is one of the most difficult problems of inorganic chemistry.

In the above account of James's work, only the more important papers have been referred to, and it is hoped that sufficient has been said to make the story comprehensible and to create a high opinion of the value of this work.

[62] C. James and D. W. Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2060; *A.*, ii, 811.

[63] C. James and A. J. Grant, *ibid.*, 1916, **38**, 41; *A.*, ii, 251.

Group I.

It was shown a few years ago that ammonium chloride and ammonium bromide are enantiotropic, with transition temperatures at 159° and 109° respectively.[64] Both these substances have been reinvestigated. In general, the cooling-curve method gives too low a value for the transition temperature, owing to the slowness at which equilibrium is established. In the case of ammonium chloride, it has been found[65] that if glycerol or mannitol is used as catalyst, the method gives excellent results, since the transition temperature given by the cooling and heating curves are in fairly good agreement. The solubilities of the salt in water between the temperatures 160° and 205° have been determined, and from these the transition temperature has accurately been calculated. If x is the number of molecules of the salt dissolved in 1 molecule of the saturated solution, then, by plotting $\log x$ against $1/T$, two straight lines are obtained, intersecting at 184·5°, which is therefore the true transition temperature for ammonium chloride. The solubility of the modification stable at lower temperatures is given by the relation $-\log x = 464{\cdot}5/T - 0{\cdot}5400$, whilst that of the modification stable at higher temperatures is given by

$$-\log x = 327{\cdot}8/T - 0{\cdot}2412.$$

In the case of ammonium bromide, the thermal method shows that the transition temperature lies between 130° and 143°.[66] The exact transition temperature was obtained by the determination of the solubilities of the salt in water between 0° and 170°. The solubility curve shows a well-defined break at 137·3°, which is therefore the true transition temperature of ammonium bromide.

The heat change involved in the transition of ammonium chloride has been determined by the calorimetric method,[67] in which weighed quantities of the salt, heated to known temperatures above and below the transition temperature of 184·5°, were introduced into a calorimeter and dissolved in the water contained therein. The heat change involved in the transformation of the α- into the β-form is -1030 calories. The theory was put forward by Wegscheider that the dissociation of ammonium chloride vapour is due to the existence of two polymorphic forms, one of which

[64] R. C. Wallace, *Centr. Min.*, 1910, 33; *A.*, 1910, ii, 208.

[65] F. E. C. Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 446; *A.*, ii, 31.

[66] A. Smith and H. E. Eastlack, *J. Amer. Chem. Soc.*, 1916, **38**, 1261; *A.*, ii, 482.

[67] F. E. C. Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1498; *A.*, ii, 431.

passes into the other under the influence of water. This theory has now been disproved.

The case of ammonium iodide presents some interest, because the crystalline habit of this salt differs from that of the bromide and chloride. It would appear probable that ammonium iodide therefore also exists in two enantiotropic modifications as well as the other two salts. Solubility determinations, however, between $-19°$ and 136° have failed to reveal the existence of a transition temperature.[68]

A new method has been described [69] of separating rubidium and cæsium, based on the solubilities of their respective alums in cold water. At 15—17°, 100 grams of water dissolve 2·3 grams of rubidium alum and 0·62 gram of cæsium alum. In order to obtain these two elements from lepidolite, the mineral is decomposed by heating it with calcium fluoride and concentrated sulphuric acid, and the resulting solution is freed from calcium sulphate and evaporated until the mixed alums crystallise. The crystals are separated and recrystallised, the mother liquor being added to the mother liquor from the first crop. The mixed liquors are then evaporated to crystallisation, and so on. After thirteen operations, the first crystals which separate are pure cæsium alum, but twenty-eight operations are necessary in order to obtain pure rubidium alum. If the mixed alums are dissolved in water, the aluminium hydroxide precipitated by the addition of ammonia, the filtrate evaporated and treated with ammonium ferric alum, the crystals which first separate are cæsium alum, and are free from rubidium. In order to separate cæsium from pollucite, the mineral is decomposed with hydrochloric acid, the silica is filtered off, and the acid filtrate is warmed after the addition of ammonium aluminium alum. On cooling, crystals of cæsium alum separate out, and after two recrystallisations a pure salt is obtained. The remainder of the cæsium may be obtained by a few recrystallisations of the mother liquor.

Some interesting work may be recorded on the nitrogeneous compounds of gold.[70] These may not only be obtained from the salts and oxides of gold and aqueous ammonia and ammonium carbonate, but also from auric hydroxide and the ammonium salts of strong acids. In general, the compounds are very explosive, and are decomposed by washing with water. It was therefore

[68] A. Smith and H. E. Eastlack, *J. Amer. Chem. Soc.*, 1916, **38**, 1500; *A.*, ii, 529.

[69] P. E. Browning and S. R. Spencer, *Amer. J. Sci.*, 1916, [iv], **42**, 279; *A.*, ii, 563.

[70] E. Weitz, *Annalen*, 1915, **410**, 117; *A.*, ii, 39.

found necessary to analyse them in the wet condition. The following details may be given. If aqueous solutions of chloroauric acid are treated with five or more molecules of ammonia, precipitates are obtained. As the amount of ammonia is increased, the quantity of chlorine in the precipitate decreases, but the ratio Au : N remains constant at 1 : 1·5. These precipitates are mixtures of two compounds,

$Au_2O_3,3NH_3$, sesquiammineauric oxide;
$NH(AuCl,NH_2)_2$, diaminoiminodiauric chloride.

The compound, $2Au(OH)_3,3NH_3$, has also been obtained. When dried in air, this compound is relatively harmless, but after drying at 105—110° or in a vacuum over phosphoric oxide, it loses water and becomes very explosive. Other compounds have been prepared with the same ratio Au : N, namely, 1 : 1·5.

If *N*/5-chloroauric acid, containing ammonium chloride, is added to a cold saturated solution of ammonium chloride saturated with ammonia, a dense yellow precipitate is formed. This compound has the formula $Au(NH_2)_2Cl,H_2O$, and has been named diaminoauric chloride, and it is not explosive. On washing with water, however, it is converted into an explosive substance, which possibly has the formula $3AuO,2NH_3,yH_2O$. Diaminoiminodiauric chloride and diaminoauric chloride each give, on continued treatment with aqueous ammonia, hydrated sesquiammineauric oxide. This substance, on heating at 115—120°, gives a very explosive black substance, diamminetriaurous oxide, $3Au_2O,2NH_3$, and with hot water it gives a still more explosive monoammineauric oxide, $Au_2O_3,2NH_3$. If *N*/5-chloroauric acid, saturated with ammonium nitrate, is added to a cold saturated solution of ammonium nitrate, and the mixture saturated with ammonia at the ordinary temperature, a precipitate is formed, which can be recrystallised from warm water. It forms colourless needles, and is tetra-ammineauric nitrate, $[Au(NH_3)_4](NO_3)_3$. This compound forms double salts with potassium, sodium, and ammonium nitrates. By double decomposition, several other salts of the radicle $Au(NH_3)_4$ have been prepared, but the hydroxide and the haloid salts have not been obtained.

The ammoniates of certain inorganic salts of silver have been described.[71] Three different methods were made use of in their preparation, namely, the absorption of ammonia by the dry salts at different temperatures, the precipitation by ether of ammoniacal-alcoholic solutions of the silver salts, and the evaporation of aqueous ammoniacal solutions of the salts. The following compounds have

[71] G. Bruni and G. Levi, *Gazzetta*, 1916, **46**, ii, 17, 235; *A.*, ii, 482, 617.

been prepared: $Ag_2O,2NH_3$, $AgF,2NH_3,2H_2O$, $AgClO_3,3NH_3$, $AgCl_4,2NH_3$, and $3NH_3,AgBrO_3,3NH_3$; $AgMnO_4,3NH_3$, $Ag_2SO_3,4NH_3$, $Ag_2SeO_3,4NH_3$, and $NH_2SO_3Ag,2NH_3$.

Pure cuprous sulphide prepared in the vacuum furnace has a melting point of $1130\pm1°$, and it does not dissociate up to a temperature of 1200°.[72] It has D_4^{25} 5·785, a value which is almost identical with that of the purest mineral sulphide. The sulphides formed by fusing together copper and sulphur are of variable composition, and always contain more sulphur than corresponds with the ratio 2Cu:S. They are, in reality, solid solutions of cupric and cuprous sulphides. Cuprous sulphide in an atmosphere of hydrogen sulphide melts at 1096°, and at 1057° in an atmosphere of sulphur vapour. This is due to the formation and solution of cupric sulphide. When cuprous sulphide is heated in an atmosphere of hydrogen sulphide at various temperatures, the sulphur content increases, there being a definite sulphur content at each definite temperature. The sulphur content increases with decrease of temperature until at 358° cupric sulphide is formed. Cuprous and cupric sulphides when heated together give similar solid solutions, and these have been found in nature. Cuprous sulphide is dimorphous, with an inversion temperature at 91°. The crystals formed by the action of ammonium sulphide on metallic copper are not cuprous sulphide, but a double sulphide of the formula $Cu_7(NH_4)S_4$ or $7Cu_2S,(NH_4)_2S$.

Group II.

A method has been described for the extraction of glucinum from gadolinite.[73] The mineral, after it has been crushed and powdered, is decomposed with concentrated sulphuric acid. The sulphates are dissolved in water and separated from the silica by decantation. The rare earths are then precipitated by oxalic acid, and the iron and glucinum in the filtrate, after the oxalic acid has been oxidised, are separated by fractional precipitation of their hydroxides by means of sodium hydroxide. The two metals are first precipitated together, and then the hydroxides are stirred with sufficient acid to dissolve about two-thirds of the whole. All the glucinum is thus dissolved, together with some iron, and this can be almost entirely precipitated by means of more sodium hydr-

[72] E. Posnjak, E. T. Allen, and H. E. Merwin, *Economic Geology*, 1915, **10**, 491; *A.*, ii, 103.

[73] C. James and G. A. Perley, *J. Amer. Chem. Soc.*, 1916, **38**, 875; *A.*, ii, 326.

oxide. The last traces of iron are removed by means of hydrogen sulphide, and the glucinum is precipitated as the basic carbonate.

The absorbent power of metallic calcium for gases is well known, and was first used by Soddy as a means of producing high vacua.[74] It appears that there are two forms of metallic calcium, an active and an inactive form.[75] The active modification begins to absorb nitrogen at 300°, and the velocity of the reaction increases with the temperature until it reaches the maximum at 440°, above which temperature the velocity decreases until it vanishes at 800°. The velocity depends on the presence of a layer of the nitride, and only reaches its maximum value after this layer has been formed. The inactive form only commences to combine with nitrogen at 800°. These two forms of metallic calcium do not appear to be allotropic modifications, but merely the metal in two different states of subdivision. When melted calcium is slowly cooled, the active form is produced, and this gives a brown nitride. The inactive form is produced by suddenly cooling calcium from 840°, and it gives a black nitride. The active form absorbs hydrogen between 150° and 300°, and above 600° calcium nitride absorbs hydrogen, carbon monoxide, carbon dioxide, and methane.

When a mixture of potassium and magnesium chlorides is electrolysed in a graphite crucible, small quantities of a black compound are found in the mass after cooling.[76] This substance evolves hydrogen when treated with water, and does not precipitate metallic nickel from an anhydrous solution of nickel chloride in alcohol, a reaction which is shown by metallic magnesium. It is not formed during the electrolysis in complete absence of oxygen, and it is believed to be magnesium suboxide.

In addition to the two well-known forms of calcium carbonate, calcite and aragonite, a third form has been described, to which the symbol $\mu CaCO_3$ has been given.[77] It is best obtained by precipitation at 60°, but it is always contaminated with calcite or aragonite; it may, however, be separated by flotation in a liquid D 2·6. The substance has D 2·54, those of calcite and aragonite being D 2·71 and D 2·88 respectively. It forms microscopic plates belonging to the hexagonal system.

The existence of calcium hydrogen carbonate as a definite compound in aqueous solution has been proved.[78] The maximum

[74] F. Soddy, *Proc. Roy. Soc.*, 1907, [A], **78**, 429; *A.*, 1907, ii, 251.

[75] A. Sieverts, *Zeitsch. Elektrochem.*, 1916, **22**, 15; *A.*, ii, 432.

[76] F. C. Frary and A. C. Berman, *Trans. Amer. Electrochem. Soc.*, 1915, **27**, 209; *A.*, ii, 33.

[77] J. Johnstone, H. E. Merwin, and E. D. Williamson, *Amer. J. Sci.*, 1916, [iv], **41**, 473; *A.*, ii, 433.

[78] A. Cavazzi, *Gazzetta*, 1916, **46**, ii, 122; *A.*, ii, 530.

quantity of calcium carbonate, which dissolves on shaking for ten hours at 0° in 1 litre of water saturated with carbon dioxide and maintained so at atmospheric pressure, is 1·56 grams, which corresponds with 2·5272 grams of calcium hydrogen carbonate. Under the same conditions at 15° there is dissolved 1·1752 grams of calcium carbonate, which corresponds with 1·9028 grams of calcium hydrogen carbonate. When carbon dioxide is passed very rapidly into lime-water saturated at 15°, the solution finally becomes clear and forms an unstable solution, supersaturated with the gas and containing 2·29 grams of calcium carbonate or 3·71 grams of calcium hydrogen carbonate in 1 litre.

Although perhaps outside the purview of this Report, yet it cannot be denied that the phosphorescence of inorganic compounds is a phenomenon of peculiar interest to the inorganic chemist, especially since it has been proved that no pure substance phosphoresces. Phosphorescence, when exhibited, is always due to the presence of an impurity, known as the phosphorogen, and the following directions have been given for the preparation of a phosphorescent calcium sulphide.[79] A mixture of 100 parts of calcium carbonate and 30 parts of powdered sulphur is heated at a dull red heat for one hour. It is then cooled and mixed with alcohol, and sufficient of an alcoholic solution of basic bismuth nitrate is added so as to give 1 part of bismuth to 10,000 parts of calcium sulphide. The mixture is dried in air and then heated at a dull cherry-red heat for two hours, after which it is slowly cooled. The bismuth, as phosphorogen, may be replaced by molybdenum, uranium, or, best, by tungsten.

Group III.

The action of nitric acid on metallic aluminium under varying conditions has been investigated.[80] The principal conclusions drawn from the work are as follows: The most important factor is the temperature, for over a considerable range an increase of 10° is sufficient to raise the rate of dissolution by 100 per cent. Next to the temperature, the concentration plays the most prominent part. The most active solvents are mixtures containing between 20 and 40 per cent. by volume of nitric acid (D 1·42). On the other hand, acids containing 94·7 per cent. nitric acid are almost without action. The presence of chlorine up to 0·05 per cent. in the nitric acid does not affect the rate of attack, but traces of sulphuric acid materially increase it. In one case it was found

[79] P. Breteau, *Compt. rend.*, 1915, **161**, 732; *A.*, ii, 100.

[80] R. Seligman and P. Williams, *J. Soc. Chem. Ind.*, 1916, **35**, 665; *A.*, ii, 435.

that 0·04 per cent. sulphuric acid was sufficient to increase the amount of aluminium dissolved from 36 to 62 mg. per 100 sq. cm. per twenty-four hours. The presence of the lower oxides of nitrogen accelerates the action, and again the metal is more readily attacked when amorphous than when crystallised. Mixtures of nitric and sulphuric acids attack aluminium very much more readily than pure nitric acid.

Many hydrates of aluminium nitrate are described in the literature beyond the one containing $18H_2O$. For example, a hydrate has been described with $15H_2O$, which is stated to be quite stable in the air.[81] In the work mentioned above, the solutions obtained often became saturated with aluminium nitrate, and gave copious crops of crystals. Three definite hydrates were recognised[82] with $18H_2O$, 15 or $16H_2O$, and $12H_2O$, which differ appreciably in habit, stability, solubility, and vapour pressure. When aluminium is kept in contact at 20° with a limited amount of nitric acid (D 1·42) very slow dissolution occurs, and the solution rapidly becomes saturated with aluminium nitrate. Large, clear, colourless crystals were deposited, but, during the handling of the supernatant liquor, it became clouded by a mass of small needles, which, on touching the original crystals, changed them also into needles. The stable form of the crystals was proved to be the known hydrate containing $18H_2O$. Saturated solutions of aluminium nitrate, made by heating the metal with nitric acid (D 1·42) and filtering through glass-wool, readily deposited the unstable crystals. These were proved to be a new hydrate containing $12H_2O$. The third hydrate was prepared as follows: The mother liquor from the hydrate containing $12H_2O$ gave, on keeping, very thin plates, some of which were very nearly 1 sq. cm. in extent. These crystals were found to contain either $15H_2O$ or $16H_2O$, but it was difficult to decide exactly the number of molecules owing to the impossibility of completely drying the crystals.

The alumina produced by the hydrolysis of aluminates is different in its properties from that precipitated on the addition of ammonia to aluminium salts in solution.[83] It is of a sandy nature and is non-hygroscopic. It has the composition $Al_2O_3,3H_2O$, and, when heated at 225°, it is converted into $Al_2O_3,2H_2O$, and at 235° it becomes Al_2O_3,H_2O. The hydroxide precipitated from aluminium salts, when dried at 80°, is approximately $Al_2O_3,2H_2O$. On heating further it loses water, and at no temperature does it appear to give a definite hydrate.

[81] M. Z. Jovitschitsch. *Monatsh.*, 1912, **33**, 16; *A.*, 1912, ii, 261
[82] R. Seligman and P. Williams, *T.*, 1916, **109**, 612.
[83] E. Martin, *Mon. Sci.*, 1915, [v], **5**, 225; *A.*, ii, 139.

When mixtures of aluminium oxide and barium carbonate in any proportions are heated at temperatures not exceeding 1500°, the aluminate, Al_2O_3,BaO, is always formed. At the temperature of the electric arc, tribarium aluminate, Al_2O_3,3BaO, is obtained from a mixture of 1 mol. of alumina and 3 mols. of barium carbonate. This compound is soluble in water. Certain other compounds are described, with the following compositions: $10Al_2O_3$,11BaO,55H_2O; Al_2O_3,2CaO; Al_2O_3,2BaS; $2Al_2O_3$,3BaS.

In last year's Report it was stated that no perborate is formed when solutions of sodium and potassium borates, with varying proportions of alkali hydroxide, are electrolysed.[84] It appears, however, that sodium perborate may readily be prepared by the electrolysis of a solution of borax containing sodium carbonate.[85] A solution of 40 grams of borax and 120 grams of anhydrous sodium carbonate is electrolysed between a platinum gauze anode and a tin tube cathode, which is bent round the anode. By the circulation of water through the cathode the temperature is kept at 18°. Using a current of 20 amperes at 6 volts, with an anode 8×6 cm., as much as 20 grams of sodium perborate were obtained in one hour.

Group IV.

A study has been made of the graphitic acids produced from various graphites.[86] The use of permanganic acid is unsatisfactory, as it gives graphitic acids of variable composition. It is preferable to use a mixture of concentrated sulphuric and nitric acids with potassium chlorate. There are two graphitic acids in leaflets, which differ in their colour and composition. Acheson, Ceylon, and Russian blast-furnace graphites give yellow graphitic acid, whilst those from Siberian, Italian, Corean, and cast-iron graphites are green. The former contain more carbon and less oxygen than the latter. The classification of graphites as intumescent and non-intumescent fails, because the artificial non-intumescent graphites give graphitic acids which are similar to those given by the intumescent natural graphites. Cast-iron graphite is an exception, since it approximates in its behaviour to the natural non-intumescent varieties. Light affects the graphitic acids, causing their colour to diminish in intensity. If washed for a long time with water, these acids are converted into a colloidal modification.

The formation of aluminium carbide from its elements has been observed at 750° and 900°, and it has been found that the com-

[84] W. G. Polack, *Trans. Faraday Soc.*, 1915, **10**, 177; *A.*, 1915, 11, 557.
[85] K. Arndt, *Zeitsch. Elektrochem.*, 1916, **22**, 63; *A.*, ii, 429.
[86] A. Lang, *Montan. Rundschau*, 1916, **19**, 1; *A.*, ii, 561.

pound is exothermic.[87] It dissociates, however, to a certain extent at 540°, since when heated in air it forms aluminium oxide and carbon dioxide. Nickel carbide, Ni_3C, is an endothermic compound, and the optimum temperature for its formation is about 2100°. It dissociates relatively rapidly at 1600° and more slowly at 900°. It must therefore be cooled rapidly if a good yield is required. Some evidence also was obtained of the direct combination of copper and carbon to give a carbide which is endothermic and dissociates rapidly at 1600°, and more slowly at lower temperatures.

Reference was made in last year's Report to the preparation of perceric potassium carbonate, $Ce_2O_4(CO_3)_2,4K_2CO_3,12H_2O$.[88] Some further work on these lines may be recorded.[89] It was not found possible to prepare the corresponding sodium salt by the method used for the potassium salt, but a solution of the corresponding ammonium salt was obtained in that way. If to this dark red solution excess of solid sodium carbonate is added and the solution evaporated in a vacuum over sulphuric acid and solid potassium hydroxide, crystals of perceric sodium carbonate are formed. The crystals are much less soluble in water than those of the potassium salt, and they effloresce in dry air. They have the formula $Ce_2O_4(CO_3)_2,4Na_2CO_3,30H_2O$. An interesting analogy between the sodium and potassium salts is shown by writing the formulæ as follows:

$$Ce_2O_4(CO_3)_2,K_2CO_3,3(K_2CO_3,4H_2O),$$
$$Ce_2O_4(CO_3)_2,Na_2CO_3,3(Na_2CO_3,10H_2O).$$

As regards the ammonium salt, although a solution of it has been prepared, it has not been found possible to obtain the salt in the solid state. The corresponding rubidium salt has been prepared by the same method as used for the potassium salt, but it has not yet been analysed.

Group V.

A convenient laboratory method has been described for the preparation of metallic vanadium, which is suitable also as a lecture demonstration.[90] Vanadyl chloride is prepared by heating a mixture of vanadium pentoxide and charcoal in a stream of chlorine, there being no need to purify it from any vanadium tetrachloride it may contain. Some of the vanadyl chloride is placed in a flask

[87] E. Briner and R. Senglet, *J. Chim. phys.*, 1915, **13**, 351; *A.*, ii, 105.
[88] C. C. Meloche, *J. Amer. Chem. Soc.*, 1915, **37**, 2338; *A.*, 1915, ii, 776.
[89] *Ibid.*, 2645; *A.*, ii, 101.
[90] R. Edson and D. McIntosh, *Trans. Roy. Soc. Canada*, 1915, [iii], **9**, 81; *A.*, ii, 143.

fitted with a platinum wire filament, which may be electrically heated. The flask should also be fitted with inlet and exit tubes for the passage of a current of dry hydrogen. The experiment should be carried out in an atmosphere of hydrogen at low pressure or in a vacuum. The platinum wire is raised to a white heat, and the metallic vanadium is deposited smoothly as a silvery-grey coating.

The crude sodium uranate obtained as a by-product in the extraction of radium from carnotite ores contains generally from 5 to 10 per cent. of vanadium pentoxide. Three methods are described, by means of which the vanadium can directly be separated from the sodium uranate.[91] By the action of hydrogen chloride the vanadium can completely be volatilised, leaving a residue of sodium uranate, sodium chloride, and uranyl chloride. From this residue, 59—64 per cent. of the total uranium can be recovered as the pure oxide, either by boiling with excess of ammonium chloride or by dissolving in dilute acid and precipitating with ammonia, and igniting the ammonium uranate produced. In all probability, by the proper regulation of temperature, hydrogen chloride would directly effect the quantitative removal of vanadium from the carnotite ores. Again, by heating the crude sodium uranate with ammonium chloride and sufficient water to form a paste, the vanadium content can be reduced to 0·5 per cent., and the uranium partly converted into oxide. The best recovery of uranium is obtained at a temperature not exceeding that necessary to volatilise the ammonium chloride and the vanadium compound. Finally, by dissolving the crude sodium uranate in the least possible quantity of hydrochloric acid, or nitric acid, or, in some cases, sulphuric acid, and boiling the solution, the vanadium is entirely precipitated, together with about 13 per cent. of the uranium. Pure uranium oxide is obtained by adding ammonia to the filtrate and igniting the ammonium uranate produced. From 58 to 79 per cent. of the total uranium can be recovered in this way when dilute hydrochloric acid or nitric acid is employed.

The method of estimation of azoimide in neutral or acetic acid solution by the measurement of the nitrogen evolved is well known, and it was noted by Raschig that the reaction is brisk and complete when the solution containing the azoimide is mixed with a slight excess of iodine and a crystal of sodium thiosulphate is added.[92] The view has been expressed that the action of the sodium

[91] H. H. Barker and H. Schlundt, *Met. and Chem. Eng.*, 1916, **14**, 18; *A.*, ii, 189.

[92] F. Raschig, *Chem. Zeit.*, 1908, **32**, 1203.

thiosulphate is due to the catalytic effect of the sodium tetrathionate, but this is not a possible explanation,[93] since neither iodine alone nor a mixture of iodine and sodium tetrathionate has any action on azoimide. The suggestion is now made that the reaction between iodine and sodium thiosulphate really takes place in two stages, the first being $Na_2S_2O_3 + I_2 = NaI + NaIS_2O_3$, and it is this intermediate compound that gives up its iodine to another molecule of sodium thiosulphate. The actual catalyst in the azoimide reaction would therefore seem to be the residue, NaS_2O_3, which takes up iodine and gives it to the azoimide or condenses to form $Na_2S_4O_6$. Since mineral acids hinder the reaction, it is advisable to add sodium acetate, owing to the fact that sulphuric acid is liberated as a by-product. Similarly, it is advisable from time to time to add a crystal of sodium thiosulphate to the solution. It is noteworthy that bromine and sodium thiosulphate have the same action on azoimide.

Although this method is accurate for relatively concentrated solutions, it does not appear to be suitable for very dilute solutions, as the end-point is reached too slowly.[94] Salts of quadrivalent cerium, such as, for example, ceric ammonium nitrate or ceric sulphate, may be used, for they immediately effect the complete oxidation of the azoimide even in very dilute solution. The reaction takes place according to the equation $2N_3H + 2CeO_2 = 3N_2 + Ce_2O_3 + H_2O$. For 0·1 gram of sodium azide about 2·3 grams of the cerium compound should be used. Free hydrochloric acid or excess of chlorine ions must be avoided, as otherwise chlorine gas will be liberated.

The reaction between azoimide and nitrous acid, which Thiele showed to take place according to the equation $N_3H + HNO_2 = N_2 + N_2O + H_2O$, has now been proved to be quantitative. The proof consisted in the addition of acetic acid to a mixture of equivalent quantities of sodium azide and barium nitrite, and in the analysis of the gases involved. The reaction can be used to estimate simple nitrites. A known excess of sodium azide is added to an acidified solution of the nitrite, then the mixture is shaken for a minute or two, rendered just alkaline by barium hydroxide, and boiled to expel the nitrous oxide, and finally acidified with acetic acid, when the excess of azoimide is estimated with iodine and sodium thiosulphate. Since nitric acid is not affected, the reaction may be used to remove nitrous acid from a mixture of the two.

When iodine is added to antimony pentachloride, reaction takes

[93] F. Raschig, *Ber.*, 1915, **48**, 2088; *A.*, 1916, ii, 98.

[94] F. Sommer and H. Pincas, *ibid.*, 1916, **49**, 1963; *A.*, ii, 97.

place, but bromine, on the other hand, has no action. Three main reactions take place according to the equations[95]:

$$SbCl_5 + I_2 = SbCl_3 + 2ICl.$$
$$2SbCl_5 + I_2 = SbCl_5,2ICl + SbCl_3.$$
$$3SbCl_5 + 2I_2 = SbCl_5,3ICl + 2SbCl_3 + ICl.$$

When less than 1·5 per cent. of iodine is dissolved in antimony pentachloride, the first reaction takes place, and there is no evidence for the existence of $SbCl_5I$ analogous to SbF_5I. The compounds $SbCl_5,2ICl$ and $SbCl_5,3ICl$ may be obtained by sublimation from a mixture of 10 grams of antimony pentachloride with 4·3 or 8·6 grams of iodine under 15 mm. pressure at 30—35°. They form bluish-black crystals melting at 62—63°, which fume in air, are readily soluble in carbon tetrachloride or chloroform, and sparingly so in antimony pentachloride. The solutions are strongly dissociated.

Nitrosulphonic acid, $HO{\cdot}SO_2{\cdot}NO_2$, sometimes reacts as if it exists in the isomeric form, $HO{\cdot}SO_2{\cdot}O{\cdot}NO$, nitrosylsulphuric acid. This suggests that both exist as tautomeric forms in concentrated sulphuric acid solution. It has been found that, if dimethylaniline in concentrated sulphuric acid solution is treated with the requisite amount of sodium nitrite, both *p*-nitro- and *p*-nitrosodimethylaniline are simultaneously formed.[96] This would seem to prove that the two forms of the acid exist together. Further, at 10—15° the yields of nitro- and nitroso-compounds are 8·33 and 71·45 per cent. respectively, and at 28—30° they are 42·85 and 39·33 per cent., which suggests that the nitro-form is favoured at higher temperatures.

Group VI.

It has usually been believed that the action of mercuric chloride on thiosulphates and polythionates is an oxidising one, owing to the fact that the white precipitate formed has been assumed to be mercurous chloride. The reaction was supposed to take place with a trithionate, for example, according to the equation:

$$Na_2S_3O_6 + 2HgCl_2 + 2H_2O = Na_2SO_4 + Hg_2Cl_2 + 2HCl + H_2SO_4 + S.$$

Further investigation has shown that the precipitate has the composition $Hg_3S_2Cl_2$, due to the combination of mercuric sulphide with excess of mercuric chloride.[97] The reactions that take place are shown by the following equations:

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O = Hg_3S_2Cl_2 + 4NaCl + 2H_2SO_4.$$
$$2K_2S_3O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 4KCl + 4H_2SO_4.$$
$$2K_2S_4O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 4KCl + 4H_2SO_4 + 2S.$$

[95] O. Ruff, *Ber.*, 1915, **48**, 2068; *A.*, ii, 144.

[96] J. Biehringer and W. Borsum, *ibid.*, 1916, **49**, 1402; *A.*, ii, 560.

[97] A. Sander, *Zeitsch. angew. Chem.*, 1916, **29**, i, ii, 16; *A.*, ii, 136.

The validity of these equations has been proved by weighing the amount of the precipitate formed in each case. The estimation of a mixture of trithionate and tetrathionate can be carried out as follows: The solution is oxidised with hydrogen peroxide in presence of a known excess of sodium hydroxide. The reactions which take place are:

$$Na_2S_3O_6 + 4H_2O_2 + 4NaOH = 3Na_2SO_4 + 6H_2O.$$
$$Na_2S_4O_6 + 7H_2O_2 + 6NaOH = 4Na_2SO_4 + 10H_2O.$$

After the oxidation is complete the unused alkali is titrated. Another sample of the mixture is heated in solution with mercuric chloride, and the acid liberated is estimated. From these two results it is easy to calculate the amounts of trithionate and tetrathionate present.

The conclusion that the formula of chromic acid is $H_2Cr_2O_7$ was arrived at by Ostwald from his observations on the freezing points of aqueous solutions of chromium trioxide, the colorimetric study of solutions of chromium trioxide, chromates, and dichromates, and from measurements of the electrical conductivity of these solutions. Some more recent spectrophotometric observations confirm this view. On the other hand, Walden, and also Abegg and Cox, favoured the formula H_2CrO_4. Some new measurements have been made of the molecular solution volumes and molecular refractivities of chromic acid, potassium chromate, and potassium dichromate.[98] The results of these measurements leave little doubt that the formula of chromic acid is $H_2Cr_2O_7$.

Mention may be made of the preparation of an interesting compound, namely, the methyl ether of the true orthotelluric acid, $Te(OCH_3)_6$.[99] The compound was prepared by adding finely powdered telluric acid to a solution of diazomethane in absolute ether. It forms white crystals, which melt at 85—87° to a limpid liquid. It is soluble in all the usual organic solvents, and, when its aqueous solution is warmed, it is partly volatile with the steam, and develops a very irritating odour.

Group VII.

Recently, a determination was made of the density of chlorine, and the value obtained for a normal litre of the gas was 3·214 grams, from which the atomic weight of chlorine is calculated to be 35·28.[1] This value is considerably below that obtained by

[98] A. K. Datta and N. Dhar, *J. Amer. Chem. Soc.*, 1916, **38**, 1303; *A.*, ii, 484.

[99] G. Pellini, *Gazzetta*, 1916, **46**, ii, 247.

[1] A. Jaquerod and M. Tourpaian, *J. Chim. phys.*, 1913, **11**, 3, 269; *A.*, 1913, ii, 401, 772.

chemical methods, and it was suggested that the divergence might possibly be due to a partial dissociation of chlorine at the ordinary temperature. In order to test this hypothesis, an investigation has been made of the vapour pressure of liquid chlorine, of the densities of liquid and saturated vapour, and of the critical constants with the view of determining whether chlorine behaves as a normal substance.[2] The chlorine was prepared by heating auric chloride, the greatest possible care being taken as regards its purity. The vapour-pressure measurements extended from $-78{\cdot}9°$ up to the critical temperature ($144{\cdot}0$), and these can be represented by the formula $\log P = A - B/T - C\log T$, in which $A = 4{\cdot}922232$, $\log B = 2{\cdot}9676491$, $\log C = 1{\cdot}8967405$, when P is expressed in atmospheres. The critical pressure was found to be $76{\cdot}1$ atmospheres and the critical density $0{\cdot}573$.

The densities of liquid chlorine may be represented by the empirical formula $d = a + b(144 - t) + c\sqrt{144 - t}$, in which $a = 0{\cdot}687014$, $b = 0{\cdot}0002379$, and $c = 0{\cdot}0622109$. The densities of the saturated vapour may also be expressed by the same formula, the values of the constants then being $a = 0{\cdot}48219$, $b = 0{\cdot}002451$, and $c = 0{\cdot}068526$. The heats of vaporisation of liquid chlorine at various temperatures have been calculated from the vapour-pressure data. The ratio of the critical density to that calculated from the simple gas laws is $3{\cdot}635$, and the value of Trouton's constant is $20{\cdot}67$. It would thus seem that chlorine behaves as a normal gas, but, at the same time, further research would seem to be advisable with regard to the low value for the weight of 1 litre of chlorine referred to above.

The degree of dissociation of bromine vapour into atoms has been determined up to temperatures in the region of 1300° by measuring the pressure exerted by a known weight of bromine vapour at a series of temperatures.[3] It was found that at the temperature of 1284° and the pressure of 721 mm., bromine is dissociated to the extent of $18{\cdot}3$ per cent.

Mention may be made of the preparation of various chlorites and a study of certain of their physical properties.[4] Certain analogies between the chlorites and nitrites are described, such as, for example, the existence of the compounds $AgClO_2,NH_3$, $AgClO_2,2NH_3$, and $AgClO_2,3NH_3$, which are similar to those formed from silver nitrite and ammonia.

By the action of a mixture of chlorine dioxide and carbon

[2] M. Pellaton, *J. Chim. phys.*, 1915, **13**, 426 ; *A.*, ii, 245.

[3] M. Bodenstein and F. Cramer, *Zeitsch. Elektrochem.*, 1916, **22**, 327 ; *A.*, ii, 552.

[4] G. Bruni and G. Levi, *Gazzetta*, 1915, **45**, ii, 161 ; *A.*, ii, 27.

dioxide, free from chlorine, on barium peroxide suspended in hydrogen peroxide solution, barium chlorite is obtained absolutely free from chloride. The sodium salt may be prepared from barium chlorite and sodium sulphate, the liquid being evaporated in a vacuum at the ordinary temperature, but the ammonium and hydroxylamine salts cannot be obtained in this way. Among the reactions described for soluble chlorites, the following may be mentioned. Potassium ferrocyanide is oxidised in acid solution to ferricyanide. With concentrated sulphuric acid, the solid chlorites deflagrate more energetically than the chlorates. Electrical conductivity measurements of potassium, silver, and barium chlorites gave for the mobility of the ion ClO_2' at 25° the mean value 51·0, which is less than that for the ion ClO_3', and less still than that for ClO_4'. Similar measurements with sodium, potassium, and silver nitrites give the mean value 75·4 for the mobility of the ion NO_2' at 25°, this being greater than that for the ion NO_3'.

It is shown that in compounds containing chlorine in different states of oxidation, the formation is the less endothermic or the more exothermic the higher the degree of oxidation.

It has been found that the action of chloric acid on iodine ions in an acid solution, resulting in the deposition of iodine according to the equation $6H^{\cdot} + 6I' + ClO_3' = 3H_2O + Cl' + 3I_2$, is greatly accelerated by the presence of ferri-ions in small concentrations.[5] The ferri-ions are converted into ferro-ions according to the equation $Fe^{\cdot\cdot\cdot} + I' = Fe^{\cdot\cdot} + I$, the ferro-ions being then oxidised thus: $6Fe^{\cdot\cdot} + 6H^{\cdot} + ClO_3' + 3H_2O + Cl' + 6Fe^{\cdot\cdot\cdot}$. The method is applicable to the separation of iodine, not merely from solutions of pure iodides, but from the brine obtained by leaching the ashes of seaweed with water. To the iodide solution, acidified with excess of sulphuric or hydrochloric acid, are added (1) potassium chlorate in the proportion indicated by the above equation, or a greater proportion if other substances capable of oxidation are present, and (2) a small volume of a solution of a ferric or ferrous salt in three times its weight of water.

E. C. C. Baly.

[5] L. Pisarshevski and N. Averkiev, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2057; *A.*, ii, 184.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

In future years it is probable that the work of reviewers in this section will be modified, and in some measure simplified, by the fact that a sister society has adopted the system of compiling annual records of progress in Applied Chemistry. This new development is to be welcomed, provided the insidious danger is avoided of making the one report purely theoretical and the other entirely technical in its treatment, and although each should make a special appeal to its own particular audience it is to be hoped that both will be based on the principle that the theoretical expansion of the subject constitutes the surest foundation for its future applications. These parallel Reports may in time be regarded as a reflection of the work progressing in the laboratory as distinguished from the factory, and may afford some index of how far these institutions are mutually supporting. To the reflective teacher they will also furnish a test of the efficiency, both in breadth and detail, of our scientific education.

In preparing the present Report the reviewer has been tempted to take shelter behind the sympathetic reference made recently in the Journal of the American Chemical Society, where it was stated that lack of perspective was an inevitable difficulty in reviewing research work annually, and that the natural tendency of the reviewers to devote special attention to the subjects in which they are particularly interested is by no means to be deplored. In the compilation of the present section of the Report very much the same difficulties were experienced as were referred to last year, and although so far as experimental work is concerned the publications reviewed under this heading have not been specially striking, it is a comforting fact that research has been by no means at a standstill. Curiously enough, considering the conditions which prevail, theoretical subjects have been prominent, and it would almost appear as if the partial cessation of orthodox laboratory work had provided an opportunity to take wider and more comprehensive views. It is to be hoped that some share of this spirit will be

apparent in the following pages, as an attempt has been made to make the Report more than a record of isolated experimental facts.

Hydrocarbons.

Under this heading the most outstanding feature of the year's publications has been the appearance of a remarkable series of papers dealing with the hydrocarbons involved in caoutchouc synthesis. Considerable space must be reserved for the discussion of this work, and consequently references to the simple hydrocarbons can only be brief.

With regard to saturated compounds, there is practically nothing to report, with the exception of the fact that Gomberg has now confirmed and extended his earlier observation that among the simpler reactions of paraffins must be included their capacity to form additive compounds with triphenylmethyl.[1] Viewed as an isolated observation, this result possesses little significance, but the question of structure at once arises, and the mode of attachment of the paraffin molecule to unimolecular triphenylmethyl becomes a matter of some importance.

As has recently been the case, however, unsaturated compounds have claimed most attention, and the many workers who have had occasion to prepare ethylene in quantity, and have observed that liquid hydrocarbons are formed to some extent during the process, will be interested in the results obtained in a detailed examination of this oil.[2] Judging from some earlier observations of Ipatiev, one might naturally suppose that these hydrocarbons owed their origin to simple polymerisation of ethylene, but further examination of the mixture has resulted in the separation of a large number of compounds in which alkylated polymethylenes predominate, a result which is highly significant in view of recent studies on the autocondensation of di-olefines. The catalytic hydrogenation of ethylene has also been studied under varying conditions, but the only point of interest which has emerged is the fact that further evidence has been accumulated showing that a factor of primary importance in such reactions is the distribution of the catalyst on a supporting medium. Thus, in some cases[3] it has been found advantageous to use infusorial earth impregnated with metallic nickel, and to pass the mixture of ethylene and hydrogen through molten paraffin in which this intimate mixture was suspended.

[1] M. Gomberg and C. S. Schoepfle, *J. Amer. Chem. Soc.*, 1915, **37**, 2569 ; *A.*, i, 28.

[2] G. de Montmollin, *Bull. Soc. chim.*, 1916, [iv], **19**, 242 ; *A.*, i, 625.

[3] J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, 1915, **37**, 2115 ; *A.*, 1915, i, 933.

Many other substances, in addition to infusorial earth, are finding application as supporting media in catalytic hydrogenation, but, considering their nature, it is more than probable that the increased efficiency to which they give rise is due to joint catalytic effects.[4] Before leaving this subject, reference may again be made to the marked influence of what are apparently insignificant changes in procedure on catalytic reactions. Thus, in the case of the addition of acetic acid to acetylene so as to form ethylidene diacetate, it has been shown that the reaction proceeds much more smoothly by forming the catalyst, which in this case consists of mercuric sulphate, in contact with the reacting materials.[5] It may be noted, however, that in the closely related case in which water is added to acetylene with the formation of acetaldehyde, the best results are obtained by varying the nature of the solvent rather than by alterations in the method of producing the catalyst.[6] These are not unexpected results, but they serve to emphasise the difficulty of identifying the real functional catalyst in any reaction.

Changes which serve as connecting links between the aliphatic and aromatic series are always worthy of attention, even when the mechanism of the processes remains obscure. The result of experiments in which paraffin-wax has been subjected to "cracking," under conditions which are not unduly drastic, seems to show that definite aromatic hydrocarbons are formed even in the absence, in the paraffin used, of constituents containing phenyl groups. It is difficult, however, taking into account questions of demand and probable costs, to agree with the claim made in the paper now under review,[7] that this process may in time form the basis of a method for producing benzene and toluene on the technical scale.

Caoutchouc.

As already indicated, a large number of publications dealing with the chemistry of caoutchouc demand detailed consideration. The papers referred to are concerned with methods of preparing doubly unsaturated hydrocarbons, the polymerisation of these substances, and the possible structural formulæ which should be allocated to the different forms of caoutchouc. To give an idea of the comprehensive nature of this work, it is perhaps sufficient to state that in one paper[8] no fewer than twenty-nine methods for the preparation of butadiene are described. These methods naturally involve some processes already known, such as the depolymerisation

[4] C. Kelber, *Ber.*, 1916, **49**, 55 ; *A.*, ii, 309.
[5] *Fr. Pat.* 475853 ; *A.*, i, 197.
[6] *Eng. Pat.*, 1915, 5132 ; *A.*, i, 465.
[7] G. Egloff and T. J. Twomey, *J. Physical Chem.*, 1916, **20**, 515 ; *A.*, i, 553.
[8] I. I. Ostromisslenski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1472 ; *A.*, i, 2.

of hydrocarbons allied to the terpenes, but a considerable number display much ingenuity, and the possible sources of butadiene have been thoroughly explored. Apart from their intrinsic importance, the reactions give an idea of the control exercised by the synthetical organic chemist in removing selected groups from compounds of diverse type. For example, the methods involve the elimination of water, halogen hydride, hydrocarbons, and acids, from open-chain or cyclic alcohols, ethers, halogen derivatives, and esters. It may be noted that three of the suggested processes start directly or indirectly from alcohol. To take one case which may in time prove to be important, the mixture of acetaldehyde and alcohol obtained by the partial oxidation of the latter by the agency of copper, undergoes further oxidation when the mixed vapours are passed over heated alumina, butadiene being then formed. The change is by no means so simple as is suggested by the equation $CH_3{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_2{:}CH{\cdot}CH{:}CH_2 + 2H_2O$, but involves no fewer than five consecutive reactions.[9] Still, the possibility of commencing one type of caoutchouc synthesis from alcohol is attractive, particularly as the method seems to be general,[10] and even admitting that the yield obtained by the above method is poor, this is a matter which will probably be improved.

The goal of Ostromisslenski's work is apparently the production, by synthetical means, of elastic colloids which display the essential physical characteristics of natural caoutchouc. With chemical standards of comparison between synthetical and natural products he is apparently little concerned. Some idea of his position is gleaned by noting his divergence from Harries in the view as to what should be included under the expressions "normal" and "abnormal" caoutchoucs.[11] The formation of ozonides, and the identification of the decomposition products to which they give rise, have in the past been made the basis of differentiation between "normal" and "abnormal" types, but the view now advocated is that a caoutchouc should be classified according to the temperatures at which the colloid acquires and loses its elastic properties, and to the range of temperature between these points. When these factors agree approximately with those determined for natural caoutchouc, the substance under examination in termed "normal." Although this may appear empirical, there is much to be said for such a view, and the effect of its adoption would be to relegate caoutchouc, and structurally related substances, to a single division of a large class of colloids which show similar physical properties.

[9] I. I. Ostromisslenski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1494; *A.*, i, 4.
[10] I. I. Ostromisslenski and P. N. Rabinovitsch, *ibid.*, 1507; *A.*, i, 4.
[11] I. I. Ostromisslenski, *ibid.*, 1374; *A.*, i, 54.

Considering the conflicting results which have been obtained by different experimenters in decomposing caoutchouc ozonides, the chemical method of classification does not seem in the meantime to be any more definite.

Despite his views on classification, Ostromisslenski does not hesitate to extend his work from the synthesis of the parent hydrocarbons to their polymerisation to caoutchouc, and the methods described by him for these conversions are apparently productive of good yields, although they add some complications to questions of structure. Thus, to take one case,[12] isoprene has been shown to undergo auto-condensation, when preserved at 80—90°, to give an open-chain dimeride termed β-myrcene. This compound contains three double linkings, two of which are in conjugated positions, and, when polymerised with barium peroxide and sodium, yields a normal caoutchouc. Curiously enough, direct polymerisation of isoprene by the same agency gives an abnormal product, the outline of the scheme being as follows:

$$2n\mathrm{C_5H_8} \longrightarrow \text{abnormal caoutchouc}$$
$$\downarrow$$
$$n\mathrm{C_{10}H_{16}} \longrightarrow \text{normal caoutchouc}$$

Obviously, the next step required to throw light on the polymerisation process was to place the structure of β-myrcene on a satisfactory basis, and to gain some idea of the magnitude of the factor n.

Although his views are largely speculative, Ostromisslenski has a strong claim, in view of his successful work, to be heard on the subject of the structure of caoutchouc, and the mechanism of its formation. Basing his arguments[13] largely on the fact that the bromide of natural caoutchouc is homologous with caouprene bromide, and is thus unicyclic, he comes to the opinion that caoutchouc itself must similarly be unicyclic, the ring containing the group $(\cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot)_x$. In this respect he does not differ from the latest conclusion arrived at by Harries. Accepting this principle,[14] we are faced with the view that, if the caoutchoucs are unicyclic, the individual molecules must consist of unusually large rings, and by its application to the formation of β-myrcene[15] and the subsequent polymerisation, a fairly clear account of the formation of normal isoprene caoutchouc can be constructed. As an initial step, isoprene may be regarded as undergoing a species of

[12] I. I. Ostromisslenski and F. F. Koschelev, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1928; *A.*, i, 274.

[13] I. I. Ostromisslenski, *ibid.*, 1932; *A.*, i, 274.

[14] I. I. Ostromisslenski, *ibid.*, 1937; *A.*, i, 275.

[15] I. I. Ostromisslenski, *ibid.*, 1941; *A.*, i, 276.

dissociation into hydrogen and a residual radicle, in which case the formation of the dimeride will follow the route shown below:

$$CH_2{:}CMe{\cdot}CH{:}CH_2 \longrightarrow H + CH{:}CMe{\cdot}CH{:}CH_2.$$

The unsaturated fragment then combines with a second molecule of isoprene, the adjustment of the valencies being effected by the new position assumed by the free hydrogen atom:

$$\underset{\times}{CH_2}{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2 \quad (\beta\text{-myrcene}).$$

Further action involves the dissociation of one of the hydrogen atoms marked × and open-chain polymerisation on lines similar to the above then proceeds until the octameride is formed, at which stage ring formation puts an end to the possibility of further complications.

It must be admitted that these theoretical ideas are somewhat crude, and suited only for blackboard demonstration. Considering current opinions as to the nature of valency and certain valuable suggestions, to which reference will afterwards be made, as to the general mechanism of addition to unsaturated molecules, the scheme outlined above must be regarded as somewhat superficial.

Numerous papers on the subject of vulcanisation have also appeared from Ostromisslenski's laboratory, and although of special interest to the technical chemist, they contain many important observations and suggestions. Harries has also contributed a paper on the same subject, but the somewhat empirical results described are beyond the scope of the Report.

The general impression left in the mind of the reviewer after a survey of the original work in this field for the past five years is that although the synthesis of a caoutchouc, identical in chemical structure and physical texture with the natural product, may never be achieved, it is evident that as a result of this work many synthetic substances possessing valuable physical properties will in time be rendered available, and will find extensive application. The development has given considerable stimulus to theory, and has revived interest in the study of hydrocarbons generally. In leaving the subject, passing reference may be made to an excellent account [16] of the past history and present position of the caoutchouc problem, which will be found useful to place in the hands of students who are making their first acquaintance with the subject.

Alcohols and their Derivatives.

So far as monohydric aliphatic alcohols are concerned, there is very little of general interest to report, most publications under this

[16] B. D. W. Luff, *J. Soc. Chem. Ind.*, 1916, **35**, 983.

heading having been confined to strictly technical inquiries. In a few cases papers have dealt with experimental methods of purifying alcohols, and more than passing interest will be attached to a brief note on the precautions to be observed in the dehydration of ethyl alcohol by metallic calcium. To those who have in the past used anhydrous alcohol purified by this agency for exact physical work, the observation that minute traces of ammonia are frequently present will not come as a surprise, and a convenient method [17] for removing this impurity by the use of alizarin and tartaric acid will be welcomed.

The hope expressed in a former Report that the whole subject of the oxidation of alcohols by catalytic methods would be systematically studied, has unfortunately not been realised, and the work has apparently been suspended. This is to be regretted, as much remains to be done in this field, and the methods now in use for the graded oxidation of even the simplest alcohols on a large scale are by no means perfect. To take a case in point, the conversion of methyl alcohol into formaldehyde under the influence of heated copper is a process which is notorious for the irregular yields and varying purity of the product obtained. One factor affecting the result is, of course, the liability of methyl alcohol to be contaminated with acetone, but leaving this out of account, the reaction is apparently by no means so simple as was at one time believed to be the case. Even when conducted at moderate temperatures, the formaldehyde liberated shows a tendency to undergo degradation to hydrogen and carbon monoxide, but at the same time, owing to polymerisation, a quantity of methyl formate is produced. These results, which have been confirmed in the course of attempts to apply the oxidation process analytically,[18] have an important bearing on some of the difficulties encountered on the technical scale. It has also been noted that the use of this metallic catalyst occasionally gives a product contaminated with copper compounds, and the suggestion has been made that this result is due to the formation of either copper formate or copper carbonyl, both of which are volatile.[19] This conclusion is probably justified, although it has been shown [20] that copper formate is easily decomposed on heating with the formation of formaldehyde. It may be remarked that methods are now available for the removal of copper compounds from formaldehyde, but it is evident that, for several reasons, copper is not an ideal catalyst for the reaction in question. The use of peroxides as oxidising media has recently found few

[17] L. W. Winkler, *Zeitsch. angew. Chem.*, 1916, **29**, 18 ; *A.*, i, 245.

[18] C. Mannich and W. Geilmann, *Ber.*, 1916, **49**, 585 ; *A.*, i, 362.

[19] H. Kunz-Krause, *Chem. Zentr.*, 1916, i, 554 ; *A.*, i, 545.

[20] K. A. Hofmann and K. Schumpelt, *Ber.*, 1916, **49**, 303 ; *A.*, i, 369.

applications, but, on the other hand, the application of ozone to the determination of the position of unsaturated linkings in alcohols continues to yield fruitful results,[21] although it is evident that, in structural work involving the formation and cleavage of ozonides, due regard must be paid to newly recognised types of decomposition undergone by these compounds.[22]

Aldehydes and Ketones.

The progress made in recent years in the study of unstable aldehydes has not been maintained in the period now under review. In fact, most recent work on aldehydes and ketones is somewhat ill-defined, and the only results which might be mentioned are extensions, on standard lines, of previous investigations or minor improvements in working processes. Amongst these may be quoted new examples of the application of Skita's method of catalytic reduction as applied to compounds possessing the carbonyl group, especially as the paper in question contains the comforting suggestion that the high pressures generally adopted by Ipatiev in such reactions are not always necessary.[23] Another example of improved practical methods is furnished by the observation that aminonitriles can be formed from both aldehydes and ketones by a simple modification of the customary procedure.[23a] Glacial acetic acid is used as the solvent for both the carbonyl compound and amine, the solution being afterwards mixed with concentrated aqueous potassium cyanide. Under these conditions, no hydrogen cyanide escapes, and the acetic acid not only promotes the condensation, but functions as a crystallising medium for the product. Suggestions of this nature are by no means trivial, as they minimise working dangers, and thereby add to the range of application of a reaction.

Polyhydroxy-alcohols.

The constitutional and experimental difficulties surrounding the synthesis of definite glycerophosphates are well known, and it will be remembered that an important advance was made two years ago, when the synthesis of α-glycerylphosphoric acid was described. The method then employed was the interaction of trisodium phos-

[21] C. Dorée and L. Orange, *T.*, 1916, **109**, 46 ; *A.*, i, 261.
[22] C. Harries, *Annalen*, 1915, **410**, 1 ; *A.*, 1915, i, 966.
[23] A. Skita and P. Stuckart, *Ber.*, 1915, **48**, 1486 ; *A.*, i, 16.
[23a] R. von Walther and R. Hübner, *J. pr. Chem.*, 1916, [ii], **93**, 119 ; *A.*, i, 559.

phate and α-monochlorohydrin; but it has now been shown that the change is by no means simple, and involves the intermediate formation of the glycide, as shown below:

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2Cl \longrightarrow OH\cdot CH_2\cdot \underset{\diagdown O \diagup}{CH}\cdot CH_2 + Na_2HPO_4 \longrightarrow OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot PO(ONa)_2.$$

It is quite apparent that this detailed study[24] of the course of the reaction does not invalidate King and Pyman's work, nor is it likely that the glycerophosphate finally produced is a mixture of steroisomerides, despite the fact that the opening of the glycide ring affords two possibilities for the subsequent addition. A considerable amount of direct and collateral evidence supports the view that the phosphate residue is attached in the terminal position, and it is interesting to note that a somewhat similar suggestion has been made by Abderhalden in order to explain the bewildering results obtained by him in his efforts to synthesise optically active fats. This particular topic has been the subject of appreciative references in past Reports, and it is satisfactory to know that steady progress is being made despite accumulating difficulties.[25] From one point of view, perhaps the most important new result now to hand in this subject is the marked difference which exists between the reactions of the active mono- and dibromohydrins. In each case, halogen may be replaced by the amino-group, but whereas an active monobromohydrin gives rise to an active aminoglycerol, similar treatment of an active dibromohydrin gives an inactive diaminohydroxypropane. The explanation offered is that the above reactions are not to be regarded as simple exchanges of groups, but involve the intermediate formation of a glycide ring from the monobromohydrin, and the consecutive production of two such rings in the case of dibromohydrin.

$$CH_2Br\cdot CHBr\cdot CH_2\cdot OH \text{ (active)} \longrightarrow CH_2Br\cdot \underset{\diagdown O \diagup}{CH}\cdot CH_2 \longrightarrow CH_2Br\cdot CH(OH)\cdot CH_2\cdot NH_2 \longrightarrow \underset{\diagdown O \diagup}{CH_2}\cdot CH\cdot CH_2\cdot NH_2 \longrightarrow NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2 \text{ (inactive)}.$$

It will be seen that the ultimate product is internally compensated, but that the adoption of a similar structural scheme would not

[24] O. Bailly, *Compt. rend.*, 1915, **161**, 677; *A.*, i, 113.
[25] E. Abderhalden and E. Eichwald, *Ber.*, 1915, **48**, 1847; *A.*, i, 8.

interfere with the production of an active aminoglycerol from monobromohydrin.[26]

The latter type of active compound is not, however, entirely proof against racemising agencies, and even when brought into reaction with metallic salts of fatty acids, totally inactive glycerol esters were obtained.

$$\left.\begin{matrix}\text{Monobromohydrin}\\ \text{or}\\ \text{Dibromohydrin}\end{matrix}\right\}\text{active} + \text{R}\cdot\text{CO}_2\text{M} \longrightarrow \left\{\begin{matrix}\text{Mono-esters}\\ \text{or}\\ \text{Di-esters}\end{matrix}\right. \quad \text{(inactive)}$$

It is highly important to note that, once the amino-group has been introduced into the glycerol molecule, ester formation without racemisation is possible by means of the sulphuric acid method, so that definite active glycerol esters have been obtained according to the scheme:

Glycerol bromohydrin $\xrightarrow{NH_3}$ aminoglycerol $\longrightarrow$ aminoglycerol ester $\xrightarrow{NaNO_2}$ glycerol ester.

In addition to the difficulties outlined above, the work has been complicated by curious optical inversions, of which the following may be taken as typical:

A. 1-Epihydrin alcohol $\nearrow$ *d*-monobutyrin.
$\searrow$ *d*-aminoglycerol $\longrightarrow$ *l*-monobutyrin.

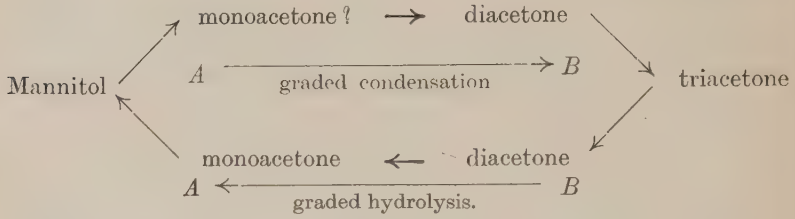
B. *d*-Epibromohydrin $\xrightarrow{HCl}$ chlorobromopropan-β-ol $\xrightarrow{KOH}$ *l*-epichlorohydrin.

Considering both types of reaction, it is evident that synthetical schemes can be constructed resembling Walden inversion cycles, and the conclusion arrived at in the original paper is that the activity of a glycerol ester always varies in sign according as the substituting group is introduced in the α- or γ-position of the parent epihydrin alcohol.

In all probability, our structural views regarding optically active polyhydroxy-compounds will be considerably affected by the study of derivatives in which selected groups are substituted. Fischer has recently turned his attention to this problem, and during the year has contributed two papers,[27, 28] which contain a number of interesting observations. He finds, for example, that the mannitol-diacetone obtained by the incomplete condensation of mannitol with the ketone is isomeric, and not identical, with the mannitol-

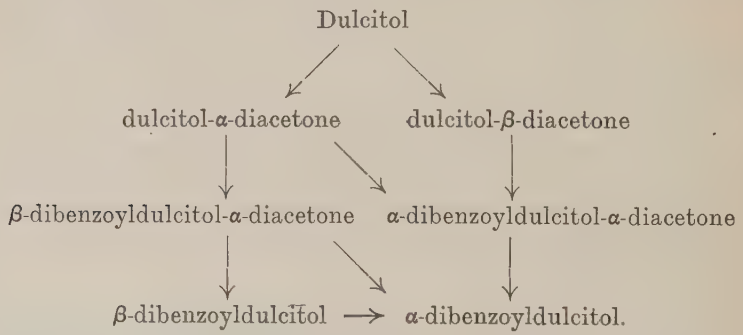
[26] See also K. Hess and H. Fink, *Ber.*, 1915, **48**, 1986; *A.*, i, 158.
[27] E. Fischer and M. Bergmann, *ibid.*, 1916, **49**, 289; *A.*, i, 364.
[28] E. Fischer and C. Rund, *ibid.*, 88; *A.*, i, 363.

diacetone which results from the partial hydrolysis of the triacetone compound.



The course of the reaction from *A* to *B* thus differs in mechanism from the reverse process, and this is in strict agreement with the views expressed by Irvine and Paterson as to the stereochemical structure of mannitol.

Another significant result is also quoted which shows that dulcitol offers similar opportunities for stereochemical study, and gives partly substituted derivatives possessing unlooked-for properties. To take a case in point, two dulcitoldiacetones are known (α and β), and the natural assumption would be that in these compounds the *iso*propylidene residues are attached to different pairs of carbon atoms. The result of benzoylation should therefore substitute the remaining hydroxyl groups, and thus preserve the isomerism; but such is not the case, as shown in the following scheme:

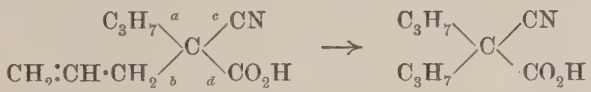


Not only does acylation obliterate the isomerism between the α- and β-diacetones, but two forms of dibenzoyldulcitol exist, one of which can be converted into the other. From these results it follows that in both α- and β-dulcitoldiacetones the same hydroxyl groups must be unsubstituted; nevertheless, the compounds are isomeric. These facts receive a ready explanation in terms of the theory that the primary hydroxyl groups in polyhydroxy-compounds, such as dulcitol, are differently arranged in space, and it may be mentioned that somewhat similar considerations have been

applied to explain the varying capacity of dibasic acids to form additive compounds.[29]

Acids and their Derivatives.

Comparatively few of the experimental results bearing on the chemistry of the aliphatic acids which have been noted during the period under review call for special mention, and thus space may be reserved under this heading for reference to important theoretical views which have been put forward in the course of the year. Meanwhile, although the subject of optical activity has been discussed at some length in recent Annual Reports, mention should be made of Fischer's renewed attempts to verify by optical methods the principle of the inter-equivalence of the four carbon valencies. The idea underlying the work[30] is that, by altering the different groups attached to an asymmetric atom so that they become identical in pairs, the equivalence of the valencies involved will be indicated by the disappearance of optical activity. Conditions were naturally selected which would be free from Walden inversion effects, so far as these perplexing possibilities can be predicted. Starting from ethyl α-cyanovalerate, the allyl group was introduced into the butyl residue, the product thereafter being converted into α-cyano-α-allylvaleric acid, which was resolved into its active forms. Reduction of the acid under mild catalytic conditions gave α-cyano-α-propylvaleric acid, which was quite inactive, thus proving the equivalence of the two valencies marked *a* and *b* in the formula shown below:

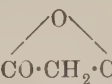


Unfortunately, the extension of the scheme to proving the equivalence of the valencies *c* and *d* failed, owing to the fact that the allyl residue participated in hydrolysis reactions which were designed to affect only the nitrile group. Topics of this nature are certainly interesting, and, as in many problems affecting compounds of simple structure, the experimental difficulties seem to have been considerable, but it may be remarked that structural evidence based on the disappearance of optical activity must of necessity be invested with some uncertainty.

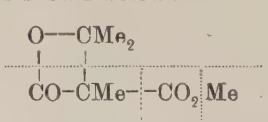
Another optical study which may be mentioned is the preparation of the active thiolmalic acids, which have been obtained by two alternative methods: (1) the action of aqueous ammonia on

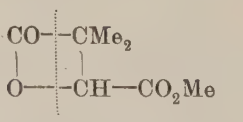
[29] T. S. Price and S. A. Brazier, *T.*, 1915, **107**, 1713; *A.*, i, 121.
[30] E. Fischer and W. Brieger, *Ber.*, 1915, **48**, 1517; *A.*, i, 11.

active xanthosuccinic acid, and (2) by the interaction of potassium hydrogen sulphide and active bromosuccinic acid.[31] By altering the conditions, the latter reaction could be varied to give different mixtures of the *d*- and *l*-product, the explanation offered, which is similar to that already put forward in the case of malic acid, being that the change may proceed directly or through the intermediate formation of the active lactone of malic acid:



Other reactions of bromosuccinic acid support in some measure Holmberg's views, but somewhat more complex possibilities are opened out by the results of another research,[32] in which it is shown that the reaction between bromosuccinic acid and pyridine bases is complex and follows an unusual course. From other sources, our knowledge regarding the lactones of the malic acid series is gradually being extended, particularly with regard to the decomposition of these compounds when heated, and a recent paper[33] furnishes an interesting result illustrating how the molecular rupture undergone by these compounds is controlled by the position of the lactonic group. The methyl ester of *as*-dimethylmaliclactonic acid, although stable enough to be distilled at the Gaede pump, suffers decomposition when boiled under 18 mm. pressure, giving rise to carbon dioxide and methyl $\beta\beta$-dimethylacrylate. On the analogy of previous work, dimethylketen and acetaldehyde might have been expected to be the essential products of the change, so that the molecular rupture evidently follows a different course, according to the position of the substituent alkyl groups, as shown below:





Of the quantitative methods available for the study of the keto-enol equilibrium, it is difficult to decide which is the most trustworthy, and the examination of oxalacetic acid by the spectrographic method[34] furnishes another example where results have been obtained which are opposed to those arrived at by the use of bromine in this determination. In the paper referred to, some ingenious suggestions are made as to the existence of hydroxy-

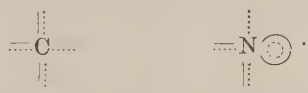
[31] B. Holmberg, *Arkiv Kem. Min. Geol.*, 1916, **6**, No. 1, 1; *A.*, i, 307.
[32] O. E. Lutz, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1549; *A.*, i, 73.
[33] E. Ott, *Ber.*, 1915, **48**, 1350; *A.*, 1915, i, 1050.
[34] A. Hantzsch, *ibid.*, 1407; *A.*, i, 12.

maleic acid as a conjugated cyclic structure, but consideration of this idea may be withheld in favour of reference to a most important contribution which has recently appeared on the general subject of unsaturation.

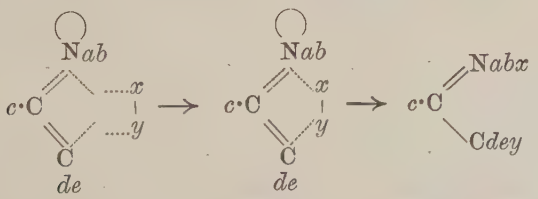
A considerable expansion of our views owes its inception to the observation that the presence of tervalent nitrogen in attachment to a doubly linked carbon atom gives rise to the properties characteristic of a conjugated system. The actual compounds which furnished this result fall within the province of another section of the Report, but the following skeleton scheme will explain sufficiently clearly the essentials of a typical reaction in illustration:

$$CHPh{:}C{-}NMe + HI \longrightarrow CH_2Ph{\cdot}C{=}NMeI.$$

Addition thus results in the formation of a methiodide, and this involves the shift of the double bond from C:C to C:N. In order to account for this divided addition to what may be regarded as the conjugated system (ethylenic carbon and tervalent nitrogen), the exercise of partial valency becomes a necessary assumption, and, as there is no good reason why such partial valencies should be restricted to any particular form of attachment, the ultimate development of this idea is the view that a unit of partial valency accompanies each normal valency. Accepting this conclusion, the carbon and nitrogen atoms may thus be represented as



so that, in a sense, each single bond may be regarded as unsaturated. It is, however, unnecessary to call into play the full number of possible partial valencies in order to explain the addition reaction now under consideration, as is seen by inspection of the diagrammatic scheme used by the authors.[35]



A preliminary union of the reactive molecules by means of partial valencies, followed by adjustment to the most stable type, completes a very simple explanation of the addition reaction. Application of the above principle of temporary addition by partial

[35] Miss E. E. P. Hamilton and R. Robinson, *T.*, 1916, **109**, 1029.

valencies is given in the original paper, and of these the most striking is perhaps the simplification of Stewart's structural representation of the maleic $\longrightarrow$ fumaric acid transformation—an example which, despite the draughtsmanship required for its reproduction, will doubtless find its way to the lecture-room. Before passing on to the applications of the ethylene–nitrogen conjugation theory to the aliphatic series, reference may be made to another important contribution[36] to the study of valency which, by a striking coincidence, appeared in the same issue of the Journal. The subject-matter of the paper in question is quite outside the scope of the present section, but this fact should not preclude an appreciative reference to a highly interesting paper which, in view of the representation of the nitrogen valencies suggested, should be read in conjunction with the two papers now under review. To resume. By application of the theory of nitrogen–carbon conjugation to ethyl β-aminocrotonate, a new light is thrown on the mechanism of the reactions of this compound and its homologues. From the ease with which the ester is hydrolysed by acids, the reasonable conclusion is drawn that the change proceeds through preliminary addition to the conjugated system.

$$\underbrace{NH_2\cdot CMe{:}CH}_{\text{conjugated}}\cdot CO_2Et \xrightarrow[HCl]{} NH_2Cl{:}CMe\cdot CH_2\cdot CO_2Et \xrightarrow[H_2O]{}$$
$$NH_4Cl + O{:}CMe\cdot CH_2\cdot CO_2Et.$$

A similar addition of ethyl iodide, followed by hydrolysis, also accounts readily for the formation of ethyl α-acetylbutyrate from aminocrotonic ester, and strong support is given to the theoretical scheme by the reactions of ethyl β-diethylaminocrotonate, $NEt_2\cdot CMe{:}CH\cdot CO_2Et$. Although non-reactive towards sodium, this ester gives additive compounds with methyl or ethyl iodides which, on decomposition with water, yield acetylpropionic and acetylbutyric esters respectively.

$$NEt_2\cdot CMe{:}CH\cdot CO_2Et + RI \longrightarrow NEt_2I{:}CMe\cdot CHR\cdot CO_2Et \longrightarrow$$
$$O{:}CMe\cdot CHR\cdot CO_2Et.$$

What is doubtless the most convincing argument in favour of these speculations is, however, furnished by the fact that, by the agency of additive reactions, an alkyl group may be attached to a carbon atom which is not coupled to hydrogen. The compound to furnish this important result was dimethyl ethylenebis-β-amino-α-methylcrotonate, which, after addition of methyl iodide and subsequent hydrolysis, was found to have undergone *C*-alkylation, despite the absence of the customary reactive hydrogen atom.

$$(CO_2Me\cdot CMe{:}CMe\cdot NH\cdot CH_2)_2 \longrightarrow 2CO_2Me\cdot CMe_2\cdot COMe.$$

[36] A. Clayton, *T.*, 1916, **109**, 1046.

With these convincing results as a foundation, it is but natural to inquire how far similar ideas extend to the reactions of ethyl acetoacetate, and the substitution of ONa for NEt_2 in the structural scheme given will show their ready application in this particular case. The further exploitation of the theory, particularly on the lines reserved in the original paper,[37] will be awaited with much interest.

Some topics of research, from the theoretical difficulties with which they are surrounded and the mass of experimental work which they involve, are not readily discussed within the limits of the Annual Reports. In such cases, the reviewer has no alternative but to direct attention at once to the original papers, and thus avoid the risk of doing scant justice to closely reasoned and sustained arguments by an imperfect synopsis. This applies with special force to the modern type of investigation on optical activity, and, in the case of recent communications[38] on the subject, little more can be done than to give a bare outline of the nature of the work. The general principles laid down by Patterson as to the form of temperature–rotation curves have been supported by the results of a new series of optical determinations conducted on the alkyl tartrates, both in the homogeneous state and in solution. In this way, a large addition has been made to the available data showing the effect of temperature and of solvents on the rotations of these compounds in light of different wavelengths. An important point which has emerged is that temperature-rotation curves may be extended in either direction beyond the limits imposed by the boiling point or melting point of the homogeneous ester by using solutions in selected solvents. The theoretical treatment of the results involves a general criticism of much that has recently been published on the causes of abnormal rotatory dispersion, and in particular on the suggestions which have been made regarding the possibility of isodynamic change in ethyl tartrate. It is extremely important to have this point settled and to secure some trustworthy method of determining when a substance is optically homogeneous, but the present position of this branch of research, if only for the reason that it is one in which experts differ and have not hesitated to argue their positions, is far from unsatisfactory even if the ultimate goal is still distant.

A considerable number of new esters have been prepared from aliphatic acids, but, for the most part, these preparations have been undertaken for pharmacological purposes and display no

[37] R. Robinson, *T.*, 1916, **109**, 1038.
[38] T. S. Patterson, *ibid.*, 1139, 1176, 1204.

novel features. Again, with regard to reactions of esters, these have, almost without exception, been studied on normal lines. Naturally enough, the Grignard reagent continues to be extensively applied to these compounds, and attention may be directed to a series of papers by Stadnikov which are important principally for the irregularity of the results obtained. Such work is of value, as it serves to throw light on the mechanism of what are usually regarded as side-reactions, and their study may possibly have the effect of making successful use of the Grignard reagent less dependent on practice and experience than is frequently the case. It may be noted that the magnesium haloid which is always present in the reagent may interfere with the reaction, owing to its tendency to react with an ester and generate a different organic haloid from that originally introduced.[39] The initial step of this type of side-reaction is indicated below:

$$R\cdot CO_2R' + MgI_2 \longrightarrow R\cdot CO_2\cdot MgI + R'I.$$

Incidentally, however, it may be mentioned that some of the variations encountered by Stadnikov apparently owe their origin to the employment of higher temperatures than are usually adopted in these reactions,[40] or may even be attributed to the method of mixing the reagents.[41]

Although reference has already been made to new ideas regarding the mechanism of syntheses based on ethyl acetoacetate, attention may at this stage be directed to some interesting results which have been obtained in attempts to synthesise hydrocarbons allied to the terpenes.[42] Condensation of chloromethyl ether and methyl sodio-α-methylacetoacetate gives the enolic product,

$$OMe\cdot CH_2\cdot O\cdot CMe{:}CMe\cdot CO_2Me,$$

from which the corresponding methoxy-β-methoxy-α-methylcrotonic acid was obtained. The decomposition of this acid by heat disengaged carbon dioxide as usual, but the reactions of the essential product showed that, as the unsaturation was preserved, it is consequently to be regarded as a butylene derivative,

$$OMe\cdot CH_2\cdot O\cdot CMe{:}CH\cdot CH_3.$$

This type of reaction is not confined to one example, and additional evidence as to the irregularity of the above substituted crotonic ester is furnished by the fact that the products of its condensation with either methyl or ethyl acetoacetates proved to be complex, and their structure is still undetermined.

An observation which is important in that it makes a valuable

[39] G. L. Stadnikov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1122; *A.*, 1915, i, 957.

[40] *Ibid.*, 2037; *A.*, i, 259.

[41] *Ibid.*, 2115; *A.*, i, 260.

[42] A. Lapworth and B. S. Mellor, *T.*, 1915, **107**, 1273; *A.*, 1915, i, 939.

reagent accessible is furnished by the discovery that aliphatic nitriles can be conveniently prepared by a simple modification of Lett's process.[43] In the particular case of acetonitrile, a catalytic method of preparation is also described[44] which is continuous in its action and gives excellent yields. The process depends on the dehydration of acetic acid and ammonia by passing the mixed vapours over alumina or thoria heated to 500°, and the success of the method suggests that it may be capable of extension to the preparation of nitriles from any saturated acid possessing the requisite volatility.

Carbohydrates.

Recent work on the sugars furnishes a striking instance of the renewal of interest in a group of compounds, the study of which was apparently on the decline. Subsequent to the time when Fischer's synthetical work in this field diminished from its first activity, there succeeded a period which naturally suffered by comparison with the brilliancy of that which preceded it. During this interval, however, much steady and valuable progress was made which has prepared the way for the present revival and for future advances, which promise to be of great importance.

During the past three or four years, the pages of the various journals bear ample testimony to the fact that research on the simple sugars is now attracting many workers (both old and new), and is showing a distinct tendency to expand. Questions of constitution are still prominent, and, as a necessary result, synthetical work is receiving a new impetus. Speaking generally, the experimental study of sugars may, at the present time, be classified under four heads: (1) investigations on the structure of reducing sugars; (2) the synthesis of partially substituted sugars; (3) the relationship between rotatory power and configuration; (4) syntheses effected by enzyme action. All these developments are affected by the recognition now given to the existence of reducing sugars in forms other than the recognised α- and β-types, and this consideration should be kept strictly in view both in reviewing old observations and in the interpretation of all new results.

It has been noted more than once in the Annual Reports that although most of the reducing sugars have been isolated in well-defined, mutarotatory forms which possess, presumably, the γ-oxidic linking, other isomerides may exist and, in certain cases, do actually exist. Thus, taking glucose as an example, the standard crystalline forms of the sugar (α and β) correspond with

[43] G. D. van Epps and E. E. Reid, *J. Amer. Chem. Soc.*, 1916, **38**, 2120.
[44] *Ibid.*, 2128.

the isomeric crystalline methylglucosides. In addition, however, two other methylglucosides have been proved to be present in the so-called "γ-methylglucoside," but so far no crystalline variety of glucose has been isolated other than the above α- and β-forms, either individually or as mixtures. The existence of no fewer than four methylglucosides shows that the parent sugar must react in four forms, in two of which the ring-forming oxygen atom does not occupy the customary γ-position.

Considering the cyclic structures possible in a hexose, it is evident that, as a maximum, there may be five isomeric glucoses in addition to the aldehydic type, each capable of existing in α- and β-forms, and similar considerations may well apply to all reducing sugars. Little systematic progress has been made during the past year in the important problems thus opened out, but a considerable amount of indirect evidence has been obtained which supports the views expressed above. Thus, Hudson and his co-workers, in the course of their investigations on rotatory power in the sugar group, isolated a second form of galactose penta-acetate,[45] and followed this up by the preparation of a third[46] and a fourth variety.[47] According to accepted views of structure, galactose should only give two non-reducing penta-acetates, but the isolation of four such compounds shows that this sugar must exist in at least four forms, and the satisfaction of having isolated the first series of crystalline derivatives corresponding with the newly recognised type of sugar isomerism thus rests with the American School.

Close inspection of some of Fischer's recent work likewise reveals evidence pointing similarly to the idea that we are only at the beginning in unravelling the complexity of even the simplest sugar molecules. Although Fischer himself is meanwhile of a different opinion, good reasons exist for the belief that the compound known as glucosemonoacetone is derived from the hypothetical "γ-glucose," and in such case it would follow that the trisubstituted sugars obtained from glucosemonoacetone would also belong to the γ-type. Trimethyl glucose was the first representative of this class, and the corresponding tribenzoyl glucose has now been isolated as the result of similar processes.[48] The new sugar is a viscous oil and displays well-marked additive properties, these features being characteristic of members of the γ-glucose

[45] C. S. Hudson and H. O. Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589; *A.*, 1915, i, 652.

[46] C. S. Hudson, *ibid.*, 1591; *A.*, 1915, i, 651.

[47] C. S. Hudson and J. M. Johnson, *ibid.*, 1916, **38**, 1223; *A.*, i, 546.

[48] E. Fischer and C. Rund, *loc. cit.*.

series, so far as these compounds have been examined. In the course of the research now under discussion, a description is given of an improved method of preparing glucosemonoacetone by cautious half-hydrolysis of glucosediacetone, but it may be remarked that the details of precisely the same method were published more than a year ago,[49] and were mentioned in last year's Report.

In view of the difficulties which will have to be faced in assigning a structure to the newly recognised varieties of sugars, it is somewhat disconcerting to find that current ideas as to the isomerism displayed by α- and β-glucose are still the object of criticism.[50] The arguments put forward by Anderson in support of the view that α- and β-glucose do not differ stereochemically, but in respect of the nature of the internal ring present in each molecule, are certainly worthy of consideration, but are opposed to much clear-cut experimental evidence to the contrary, and may thus, meanwhile, be held in reserve. Another paper[51] involving structural considerations to which attention should be directed contains a number of valuable experimental results bearing on the configuration of sugars containing more than six carbon atoms. The work in question is undoubtedly of a high order, but in clearing up some points has had the effect of adding confusion to others. This is not so much the fault of the investigator as of the totally inadequate nomenclature with which the chemist in this field is equipped, or rather handicapped. As a general rule, the first of several possible isomeric sugar derivatives isolated is promptly termed the α-form. If, in the course of time, a second and third isomeride are obtained, these become known as the β- and γ-forms, irrespective of the fact that the index letters α and β refer to definite stereochemical isomerides and have a restricted application. Thus, Pierce obtained a new variety of mannoheptoic acid, which is termed the β-form, for no better reason than that it is the second such compound to be isolated. There may not be any real objection to this, but the sugar obtained from it is likewise termed a β-sugar, which is probably not the case.

So much synthetical work on the sugars is based on the use of tetra-acetyl bromoglucose that it is a matter of some importance to have full details of a good working method for the preparation of this valuable reagent. For many years Fischer has prepared the compound as the result of two separate reactions; first, the formation of penta-acetyl glucose, followed by the conversion of this

[49] J. C. Irvine and J. L. A. Macdonald, *T.*, 1915, **107**, 1701; *A.*, i, 17.
[50] E. Anderson, *J. Physical Chem.*, 1916, **20**, 269; *A.*, i, 465.
[51] G. Pierce, *J. Biol. Chem.*, 1915, **23**, 327; *A.*, i, 18.

compound into the bromo-derivative by the action of hydrogen bromide dissolved in glacial acetic acid. He now gives a complete account of the method,[52] but it may be remarked that the process which has proved so conspicuously successful in the hands of Hudson and his collaborators possesses many advantages. Instead of two stages, one is sufficient, in that the reagent used—a solution of hydrobromic acid in acetic anhydride—effects simultaneous acetylation and bromination. Many examples might be quoted to illustrate the convenience and efficiency of the method which, as recently described,[53] applies with equal facility to pentoses.[54]

Considerable interest is attached to the partial acylation of polyhydric alcohols and sugars, which is now engaging the attention of Fischer.[55, 56] These compounds have been prepared by the general methods described by Irvine and Scott in the case of reducing sugars, and by Irvine and Paterson for polyhydric alcohols, and as few new examples have recently been added to the list of partially substituted glucoses, most of the results are thus described elsewhere.

Although the generalisations established by Hudson regarding the relationship between rotatory power and constitution in the sugar group were first applied to simple glucosides, it has recently been shown in numerous cases that the principle extends to acetylated aldoses of different types, and even to the monobasic acids allied to the sugars.[57] A further important observation is that the rule holds approximately in the case of acetylated derivatives of amino-sugars, thus indicating that the nature of the groups in the sugar chain has a relatively small effect on the rotation of the terminal asymmetric system.[58] One result of this line of work has been the preparation of a large number of acetylated sugars, and the introduction of many improvements in the methods of preparing and purifying these compounds.[59] The results obtained in the optical study of these compounds confirm Hudson's views, and in cases where experimental values are not in agreement with the rule, it is probable that this is due to the derivatives under examination being related to entirely different forms of the parent

[52] E. Fischer, *Ber.*, 1916, **49**, 584; *A.*, i, 373.

[53] J. K. Dale, *J. Amer. Chem. Soc.*, 1916, **38**, 2187.

[54] J. K. Dale, *ibid.*, 1915, **37**, 2745; *A.*, i, 117.

[55] Part II, E. Fischer and C. Rund, *loc. cit.*

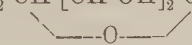
[56] Part III, E. Fischer and M. Bergmann, *loc. cit.*

[57] P. A. Levene, *J. Biol. Chem.*, 1915, **23**, 145; *A.*, ii, 3. See also P. A. Levene and G. M. Meyer, *ibid.*, **26**, 355; *A.*, ii, 545.

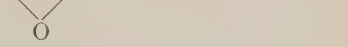
[58] C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, 1916, **38**, 1431; *A.*, i, 597.

[59] See also C. S. Hudson and D. H. Brauns, *ibid.*, 1915, **37**, 2736; *A.*, i, 118; C. S. Hudson and J. M. Johnson, *ibid.*, 1915, **37**, 2748; *A.*, i, 117.

sugar. Incidentally, in the course of this work a number of important observations have been made. Thus, starting from tetra-acetyl fructose, for which a simple method of preparation is described, a new form of fructose penta-acetate is obtained by the action of acetic anhydride containing zinc chloride. It is a curious fact that the two isomeric fructose penta-acetates so far known are not interconvertible by the action of zinc chloride, and it is quite possible that they are derived from different types of fructose. The chemistry of fructose will no doubt be considerably expanded by the use of tetra-acetyl fructose, and the reagent has already been turned to good account in the preparation of a crystalline variety of methylfructoside.[60] There is little doubt that fructose shows a pronounced tendency to exist in reactive forms similar to "γ-glucose," in which the ring-forming oxygen is connected to a carbon atom other than that in the γ-position. Thus it has been shown[61] that the syrup originally isolated by Fischer by the condensation of fructose with methyl alcohol contains two distinct methylfructosides of different type. One of these compounds resembles the α- or β-methylglucosides, and fails to react with acetone, but the other enters into ready condensation with the ketone, and is, in addition, characterised by the ease with which it reduces permanganate. The existence of these distinct fructosides clearly indicates that the parent sugar can react in at least four forms, the most probable structures of which are shown below:



Fructose of normal type.



Fructose of the ethylene-oxide type.

Additional evidence pointing to the idea that fructose shows a ready tendency to react in forms other than the standard α- and β-varieties is afforded by the somewhat complicated results recently obtained in a study of the conductivity changes shown during the mutarotation of fructose dissolved in boric acid.[62]

Brief reference was made in last year's Report to a new and convenient method devised by Weerman for degrading sugars to lower members. Fuller details of the working methods employed,

[60] C. S. Hudson and D. H. Brauns, *J. Amer. Chem. Soc.*, 1916, **38**, 1216; *A.*, i, 547.

[61] J. C. Irvine and G. Robertson, *T.*, 1916, **109**, 1305.

[62] J. Böeseken, A. H. Kerstjens, and C. E. Klamer, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1654; *A.*, i, 596.

and their range of application, are now available, and a few characteristic cases in which the method has been used successfully are noted below.

1. *d*-Glucose ⟶ *d*-arabinose.
2. *d*-Galactose ⟶ *d*-lyxose.
3. *l*-Mannose ⟶ *l*-arabinose.
4. *l*-Arabinose ⟶ *l*-erythrose.

In the experience of the writer of this Report, the reactions involved[63] proceed with the utmost smoothness, and constitute a great improvement on the methods hitherto in use.

Among isolated observations which are of interest, the extension to pentoses of the method of resolving racemic sugars through the agency of optically active mercaptals may be noted,[64] and in view of the number of successful applications of this process it may now be regarded as general in its application. Turning to an entirely different subject, an observation which may in time prove to be highly important is that the oxidation of glucose by means of alkaline potassium permanganate is apparently assisted by atmospheric oxygen. This result is not altogether unexpected, but does not seem likely to lead to any improvement in the methods available for oxidising sugars to the corresponding monobasic acids, although it may afford a clue to the mechanism of natural processes in which the sugars are converted into their ultimate oxidation products.[65]

Although amino-sugars are few in number, they never lose in interest. The complex problems connected with the constitution of these compounds are now being studied by Levene, who is engaged on a systematic investigation which has as its object the determination of the configuration possessed by glucosamine. The work has not proceeded far enough for definite conclusions to be drawn, but has resulted in a considerable extension of our knowledge of the amic acids related to the amino-aldoses.[66, 67] Incidentally, this work has confirmed a point of fundamental importance in this section of sugar chemistry, in that the suggestion already made that compounds of the type of glucosimine are in reality amino-glucosides, has been confirmed, and has been shown to be equally applicable to imines of the pentose series.[68] Among other

[63] R. A. Weerman, "Over de inwerking van natrium hypochloriet op amiden van onverzadigde zuren en oxyzuren," *Dissertation, Delft*, 1916.

[64] E. Votoček and V. Vesely, *Zeitsch. Zuckerind. Böhm.*, 1916, **40**, 207; *A.*, i, 308.

[65] E. J. Witzemann, *J. Amer. Chem. Soc.*, 1916, **38**, 150; *A.*, i, 372.

[66] P. A. Levene, *J. Biol. Chem.*, 1916, **24**, 55; *A.*, i, 203.

[67] P. A. Levene and F. B. La Forge, *ibid.*, 1915, **22**, 331; *A.*, 1915, i, 944.

[68] P. A. Levene, *ibid.*, 1916, **24**, 59; *A.*, i, 201.

results recently to hand on this subject may be noted the fact that chondrosamine and a lyxohexosamine prepared synthetically yield the same osazone, and, further, that the corresponding amino-acids give the same anhydromucic acid on oxidation.[69] The difficulties which usually attend the allocation of the amino-group in these compounds may in some measure be removed by taking advantage of generalisations regarding the rotations of epimeric hexosamic acids, and the further extension of Levene's work will be closely followed.[70]

It is a remarkable fact that doubt still exists as to the origin of amino-sugars such as glucosamine, and as to the condition in which these compounds exist in the complexes from which they are obtained by hydrolysis. The recent isolation of natural glucosamine glucosides from certain fungi seemed to indicate that compounds of similar type would be widely distributed and readily identified, but a careful examination[71] of *Boletus edulis* has given results showing that the glucosamine formed on hydrolysis owes its origin to complexes of the glucoprotein type, and not to preformed glucosamine glucosides. Further work in this field will, therefore, doubtless be focussed on the isolation of glucoproteins of definite composition.

As indicated in last year's Report, work on the synthesis of glucosides by means of the action of enzymes has recently shown a distinct falling off, but the new literature on this subject is still fairly extensive. Among recent results of importance may be mentioned the synthesis of a galactobiose[72] by the autocondensation of galactose under the influence of emulsin. Considering the fact that we are still far from a complete understanding of the linkings present in even the simplest disaccharides, it is unfortunate that the new sugar, which is apparently different from the galactobiose already described, has only so far been obtained as a syrup, and thus its detailed examination has naturally been restricted.

Although exact studies on the selective hydrolysis of either glucosides or compound sugars ought to be conducted with enzymes which have been purified from closely related forms, it would appear that drastic purification is unnecessary in the case of syntheses effected by enzymes.[73] It must be admitted that the synthetical action of enzymes has in the past few years led to many notable achievements, particularly in cases to which ordinary

[69] P. A. Levene, *J. Biol. Chem.*, 1916, **26**, 143 ; *A.*, i, 712.
[70] *Ibid.*, 367 ; *A.*, ii, 546.
[71] Miss W. Ross, *Biochem. J.*, 1915, **9**, 313 ; *A.*, 1915, i, 1084.
[72] E. Bourquelot and A. Aubry, *Compt. rend.*, 1916, **163**, 60 ; *A.*, i, 596.
[73] *Ibid.*, 1915, **161**, 463 ; *A.*, 1915, i, 1076.

processes are inapplicable, but despite this success the synthesis of sucrose still remains unaccomplished,[74] and, considering recent views as to the structure of sucrose, this negative result is not surprising.

The analytical applications of enzyme action might perhaps be dealt with more appropriately in another section of the Report, but attention should be directed generally to the steady improvement, both as regards accuracy and range of application, of methods whereby, through the use of selected enzymes, specific sugars can be estimated even when they are mixed with closely related substances. A good account of such a method is furnished by Davis,[75] who has shown, among other cases quoted, that raffinose may be estimated by enzymotic hydrolysis. By a curious coincidence, practically the identical method was described about the same time from another source.[76]

Disaccharides.

The hydrolytic process referred to above, in which raffinose is degraded to melibiose and fructose, has been utilised for the preparation of the disaccharide on a large scale. The working details show that the process proceeds smoothly, and thus another example[77] has been added to the already lengthy list of excellent preparations in the sugar group, which we owe to the American chemists.

From the theoretical point of view, two important contributions have been made during the year to the chemistry of disaccharides. The first refers to the identification of numerical relationships between the molecular rotation of a disaccharide of the sucrose group and those of the α- and β-forms of the aldose produced on hydrolysis. The interesting, but somewhat intricate, generalisation thus established can only be properly appreciated by reference to the original paper,[78] and, no doubt, its future development will be awaited with much interest.

As a result of observations described in a recent paper,[79] current views on the constitution of sucrose are largely overthrown. The fact that invert-sugar consists of an equimolecular mixture of glucose and fructose has been too readily accepted as evidence that

[74] W. Löb, *Biochem. Zeitsch.*, 1916, **72**, 392; *A.*, i, 296.

[75] *J. Soc. Chem. Ind.*, 1915, **35**, 201; *A.*, ii, 202.

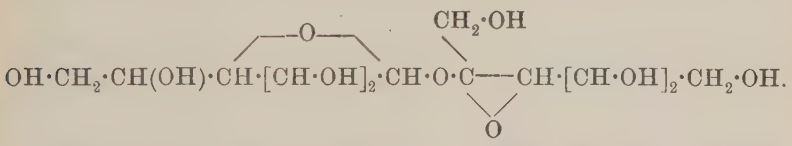
[76] C. S. Hudson and T. S. Harding, *J. Amer. Chem. Soc.*, 1915, **37**, 2193; *A.*, 1915, ii, 803.

[77] *Ibid.*, 2734; *A.*, i, 120.

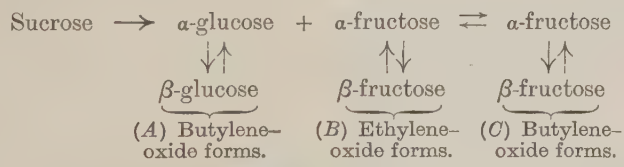
[78] C. S. Hudson, *ibid.*, 1916, **38**, 1566; *A.*, i, 630. See also C. S. Hudson and R. Sayre, *ibid.*, 1867; *A.*, i, 711.

[79] W. N. Haworth and J. Law, *T.*, 1916, **109**, 1314.

the forms of the sugars thus isolated are of necessity the forms in which they are combined in the disaccharide. On the contrary, direct hydrolysis of sucrose affords little or no evidence as to the constitution of the constituent hexoses, but a rigid proof has now been supplied by a study of the hydrolysis of fully methylated sucrose. Octamethyl sucrose has now been obtained in the pure state in considerable quantity, and gives, when treated with dilute acid, tetramethyl glucose and tetramethyl fructose, in which the linkings are of necessity preserved exactly as in the parent disaccharide. The methylated aldose actually isolated proved to be the characteristic tetramethyl glucose of the butylene–oxide type, thereby confirming a previous result, but, on the other hand, the ketose displayed a rotatory power and reaction towards permanganate which at once stamped the compound as being allied in structure to "γ-glucose." A new formula for sucrose is thus indicated, which accounts not only for the extreme ease with which the disaccharide is hydrolysed, but also for previous failure to effect its synthesis. This provisional formula shows a butylene–oxidic aldose coupled to an ethylene–oxidic ketose through their reducing groups:



Accepting this view, the hydrolysis of sucrose becomes an exceedingly complex change, best represented by a diagrammatic scheme, which shows how the sugars liberated on hydrolysis not only undergo mutarotation, but, in the case of fructose at least, change from one type to another:



The final products consist essentially of the equilibrium mixtures (*A*) and (*C*) together, probably, with a small proportion of (*B*).

The importance of the advance which has been made in the study of the most interesting of all sugars, and the new lines of work thus opened out, will be fully realised.

Polysaccharides.

It is probably only right that much of the work in this group remains physical rather than chemical in character, for there is much still to be learned as to the effect of surface conditions in modifying chemical changes when dealing with complexes of high molecular weight and sparing solubility. This is borne out in much of the recent work on the chemistry of starch, where, to take a case in point, the formation of the so-called crystalline starch [80] is in all probability due to the precipitation of the colloid by the action of traces of mineral salts.[81] The influence of surface conditions is probably also responsible for the distinct difference which has been noticed in the relative ease with which cellulose and starch may be acetylated, and in the effects which different catalysts have on the reaction.[82]

The examination of starch by purely chemical methods has also yielded interesting results, and at least one element of confusion has been removed in the course of two recent investigations [83, 84] dealing with the phosphorus-containing constituent. The idea seems to have prevailed that the starch complex contains an unstable fragment, in which phosphoric acid is combined, and that this is the first portion of the molecule to be removed on hydrolysis. Such is not the case, as during the degradation of starch with 10 per cent. hydrochloric acid the unhydrolysed residue contains most of the combined phosphorus. In fact, there are good reasons for the belief that a definite compound will in time be isolated which would represent the carbohydrate phosphate originally present in the starch complex. The results of the paper now under review are not inconsistent with Samec's observation that the removal of the phosphorus constituent is the initial action when starch is decomposed with alkalis.

Naturally enough, most recent investigations on cellulose have had a direct technical bearing, and there does not appear to be any necessity to refer to them, as no points of general theoretical importance have been noted.

[80] M. W. Beyerinck, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 305; *A.*, 1915, i, 940.

[81] W. Harrison, *J. Soc. Dyers*, 1916, **32**, 40; *A.*, i, 251.

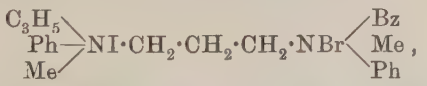
[82] J. Böeseken, J. C. van den Berg and A. H. Kerstjens, *Rec. trav. chim.*, 1916, **35**, 320; *A.*, i, 308.

[83] M. Samec, *Koll. Chem. Beihefte*, 1916, **8**, 33; *A.*, i, 308.

[84] J. H. Northrop and J. M. Nelson, *J. Amer. Chem. Soc.*, 1916, **38**, 472; *A.*, i, 373.

Nitrogen Compounds.

Most of the experimental researches of the past year which can be suitably reviewed under this heading deal with topics which are being expanded on normal lines, and there is little that can be said regarding such publications except to indicate isolated observations which may lead to useful improvements in working methods. Purely theoretical subjects have not been neglected, and reference has already been made to papers which deal with the valencies of nitrogen, particularly with regard to the formation of conjugated systems when tervalent nitrogen is linked to ethylenic carbon. In addition, several other theoretical papers have appeared in which explanations are offered as to the mechanism of reactions conducted on nitrogen compounds, although it is unlikely that such views will find immediate or widely spread application.[85] The possibility of gleaning fresh information as to the distribution of nitrogen valencies through the study of optically active compounds still continues to receive attention, but efforts to isolate substances containing two similarly asymmetric nitrogen atoms in active forms analogous to the tartaric acids have led to no positive result. Even a modification of this idea, in which the attempt has been made to resolve a system containing two nitrogen atoms of unlike asymmetry, has likewise proved fruitless, as, although a compound of the desired type has been obtained, no resolution was effected.[86] The test substance selected for these experiments was



and failure in this case, where the nitrogen atoms are separated by a chain of carbon atoms, lends support to the belief that the solution of the original problem will not be realised considering the difficulty (or, it may be, the impossibility) of forming a compound containing two directly linked quinquevalent nitrogen atoms.[87]

The double salt formulated above was isolated in two stereoisomeric forms, and further examples illustrating the inexhaustible capacity of nitrogen compounds to form such isomerides is furnished by a study of substances which contain two >C:N groups.[88] Starting from the esters of carbazinic acid, alkylidene

[85] G. Povarnin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 989 ; *A.*, 1915, ii, 761.
[86] E. Wedekind and T. Goost, *Ber.*, 1916, **49**, 942 ; *A.*, i, 671.
[87] B. K. Singh, *T.*, 1916, **109**, 780 ; *A.*, i, 757.
[88] M. Busch, *J. pr. Chem.*, 1916, [ii], **93**, 25 ; *A.*, i, 338.

derivatives were obtained by condensation with aldehydes, and the products were thereafter decomposed with alcohols.

$$NH_2\cdot NH\cdot CS_2R' \longrightarrow CHR{:}N\cdot NH\cdot CS_2R' \longrightarrow CHR{:}N\cdot N{:}C(SR')\cdot SR''.$$

In one case studied, all four possible stereoisomerides were isolated, and it may be noted that the last stage of the reaction affords ample scope for applying variations of Robinson's theory of conjugated systems involving tervalent nitrogen.

Reactions of Simple Nitrogen Compounds.

A considerable amount of work has been devoted to developing improvements in practical methods, and in some cases where these do not include any theoretical advances, it seems desirable to refer to them, if only briefly. Thus, the method of alkylating amines or imino-compounds by the agency of aldehydes in the presence of an oxidisable compound has been extended considerably in scope and otherwise improved.[89] To take another case of improved working processes, the observation[90] that *aci*-trinitromethane, in the form of the potassium salt, is easily produced by the interaction of tetranitromethane and potassium ferrocyanide will exclude the older method of preparation, which, even in experienced hands, proved to be extremely dangerous.

After a period of successful use as a reagent, diazomethane has recently been but little employed, although it may be mentioned that its action on aromatic acyl chlorides has been shown to be very similar to that on aldehydes, and gives rise to chloromethyl chlorides.[91]

$$R\cdot COCl + CH_2N_2 \longrightarrow R\cdot CO\cdot CH_2Cl.$$

At the same time, the application of diazomethane as a methylating agent is evidently more restricted in scope than was at one time imagined. Hydroxyl groups of all types, and even carboxyl groups, are occasionally unaffected by the reagent, so that much research of a fundamental nature remains to be done before its use in structural work will be fully assured. In the case of tyrosine,[92] the failure of diazomethane to methylate the carboxyl group is probably due to the existence of a betaine ring in the molecule, and it may be remarked, incidentally, that there is a growing tendency to make use of cyclic structures containing quinquevalent nitrogen to explain reactions of simple compounds. Even in the case of guanidine, the suggestion has been put for-

[89] *D.R.-P.*, 287802; *A.*, i, 326. *D.R.-P.*, 291222; *A.*, i, 554. *U.S. Pat.*, 1158496; *A.*, i, 326.

[90] F. D. Chattaway and J. M. Harrison, *T.*, 1916, **109**, 171; *A.*, i, 245.

[91] D. A. Clibbens and M. Nierenstein, *ibid.*, 1915, **107**, 1491; *A.*, 1915, i, 1062.

[92] A. Geake and M. Nierenstein, *Biochem. J.*, 1915, **9**, 309; *A.*, 1915, i, 1060.

ward that the reactions of the compound are best expressed in terms of such a cyclic structure,[93] and although this is not opposed to many reactions of the compound, including its failure to give a positive result in the ninhydrin reaction,[94] it apparently does not affect the deductions drawn by Levene and Senior as to the position occupied by the two amino-groups in divicine.[95]

Amino-acids and Proteins.

Although research on amino-acids is once more reviving, there is still little tendency to work with active products, and the numerous papers dealing with this subject, although contributing much valuable information, have not been fundamental in character, and are thus somewhat difficult to discuss. So far as synthetical methods are concerned, little of importance has been noted, but mention may be made of the formation of glycine from methyl cyanoacetate by a series of reactions involving the production of cyanoacetylazide, $CN{\cdot}CH_2{\cdot}CO{\cdot}N_3$, decomposition of this with alcohol, and hydrolysis of the product. As a method of preparing glycine, the reaction is of no importance, but is interesting as, taken in conjunction with the usual synthesis of the amino-acid from chloroacetic acid, it constitutes an indirect proof of the interequivalence of the four carbon valencies.[96]

A considerable amount of work has been expended in studying the effect of nitric acid on piperazine derivatives.[97] It is shown, as a result of these investigations, that nitric acid acts as an oxidising agent on 3 : 5-diketo-1-methylpiperazine,

$$NMe\begin{<}CH_2{\cdot}CO\\CH_2{\cdot}CO\end{>}NH,$$

so as to generate the corresponding tetraketone, and that this type of reaction seems to be general save when substituents are introduced into the two methylene groups. Thus, the imide obtained from dimethyl iminodipropionate was not oxidised, but underwent nitration when treated with nitric acid, as shown below:

$$NH\begin{<}CHMe{\cdot}CO\\CHMe{\cdot}CO\end{>}NH \longrightarrow NO_2{\cdot}N\begin{<}CHMe{\cdot}CO\\CHMe{\cdot}CO\end{>}NH.$$

It is unfortunate that the above imide was obtained only in small amount, as the further effect of nitric acid on the compound is a subject which might well be expected to yield interesting results.

[93] H. Krall, *T.*, 1915, **107**, 1396 ; *A.*, 1915, i, 946.

[94] V. J. Harding and R. M. MacLean, *J. Biol. Chem.*, 1916, **25**, 337 ; *A.*, ii, 459.

[95] P. A. Levene and J. K. Senior, *ibid.*, 607 ; *A.*, i, 678.

[96] A. Darapsky and D. Hillers, *J. pr. Chem.*, 1916, [ii], **92**, 297 ; *A.*, i, 127.

[97] J. V. Dubsky and pupils, *Ber.*, 1916, **49**, 1037, 1041, 1045 ; *A.*, i, 635, 672, 636.

Despite the uncertainties which attend reactions carried out either on amino-acids or on glycerol at comparatively high temperatures, work involving these possibilities continues to meet with success. In addition to the positive results previously obtained in attempts to synthesise *cyclo*-glycylglycines by the somewhat drastic method of heating an amino-acid with glycerol, it is satisfactory to note that mixtures of amino-acids react with equal facility to give mixed *cyclo*-anhydrides, of which *cyclo*-alanylglycine may be taken as a typical example.[98] Greater interest will, however, be taken in a recent communication from Abderhalden's laboratory, which describes an ambitious synthesis,[99] the ultimate object of which is the production of polypeptides of high molecular weight so as to study the action of specific ferments and to determine the simplest molecular structure displaying colloidal properties. Standard methods were employed in the synthesis, and as the essential reagent used was *d*-bromo*iso*hexoyldiglycylglycyl chloride, the coupling reactions rapidly gave a polypeptide containing nearly a hundred atoms, the molecular weight of which is more than 1200. It is surprising that the optical activity survived the reactions. As the uncertainties attending racemisation or Walden inversion effects have in recent years greatly restricted synthetical work on active amino-acids and polypeptides, this revival will be welcomed, particularly as the work has a definite objective.

With regard to proteins, there is little to note in this section. The application of a drastic cleavage method involving the use of nitric acid does not seem to be advantageous save in special cases, as, for example, the identification of phenylalanine through its conversion into the easily recognisable *p*-nitrobenzoic acid.[1] Among other results which have been obtained by the treatment of proteins with powerful reagents, the most interesting is the observation that, by the action of bleaching powder, proteins are converted into derivatives containing the NCl group, the presence of which confers germicidal properties on the product. It would also appear that both proteins and amino-acids react with chloroamines,[2] aldehydes being generally formed under these conditions, and work of this nature may possibly afford a clue to the antiseptic action of chloroamines or may in time be applied in structural work on the proteins.[3]

JAMES COLQUHOUN IRVINE.

[98] L. C. Maillard, *Ann. Chim.*, 1915, [ix], **4**, 225 ; *A.*, i, 505.

[99] E. Abderhalden and A. Fodor, *Ber.*, 1916, **49**, 561 ; *A.*, i, 375.

[1] C. T. Mörner, *Zeitsch. physiol. Chem.*, 1915, **95**, 263 ; *A.*, i, 512.

[2] H. D. Dakin, J. B. Cohen, M. Dufresne, and J. Kenyon, *Proc. Roy. Soc.*, 1916, [*B*], **89**, 232 ; *A.*, i, 533.

Part II.—Homocyclic Division.

Reactions.

During the past year or two several novel reactions have been devised. In one, amines are oxidised to aldehydes by hydrogen peroxide in the presence of iron, typical examples being the conversion of ethylamine into acetaldehyde and of benzylamine into benzaldehyde.[1] In another, aromatic aldehydes are prepared by the action of carbon monoxide on the parent hydrocarbon, under a pressure of 50—90 atmospheres, in the presence of aluminium chloride; benzaldehyde, *p*-tolualdehyde, and *p*-chlorobenzaldehyde have been made in this manner.[2] The introduction of the amino-group into aromatic compounds has been effected by condensation with hydroxylamine in presence of sulphuric acid.[3] Sulphonic acid or nitro-groups of aromatic hydrocarbons can be replaced by chlorine, in many cases quantitatively, by the action of thionyl chloride at moderately high temperatures; thus at 160—180° *p*-chlorobenzenesulphonic acid yields *p*-dichlorobenzene and nitrobenzene yields chlorobenzene.[4]

α-Arylamino-nitriles may be conveniently prepared by leaving a solution of an aldehyde or ketone and the amine in glacial acetic acid with concentrated aqueous potassium cyanide; thus, for example, *o*-nitrobenzaldehyde and aniline yield *o*-nitro-α-anilinophenylacetonitrile, $NO_2 \cdot C_6H_4 \cdot CH(NHPh) \cdot CN$.[5] By the action of diazomethane on acyl chlorides chloromethyl ketones are obtained[6]:

$$R \cdot COCl + CH_2N_2 \longrightarrow R \cdot CO \cdot CH_2Cl.$$

Nitration.—In continuation of the work on the relative velocity of substitution caused by the halogen elements, chlorine, bromine, and iodine,[7] comparison of the directive influences of fluorine and chlorine has now been made, and it is found that in the nitration of *p*-fluorochlorobenzene the nitro-group enters the ortho-position with respect to the chlorine atom to the extent of 62·25 per cent.

[1] K. Suto, *Biochem. Zeitsch.*, 1915, **71**, 169; *A.*, 1915, i, 941.

[2] J. Longman, *Eng. Pat.*, 1915, No. 3152; *A.*, i, 315.

[3] J. F. dé Turski, D.R.-P., 287756; *A.*, i, 313.

[4] H. Meyer, *Monatsh.*, 1915, **36**, 719, 723; *A.*, i, 134, 135; compare also Kinzlberger & Co., D.R.-P., 280739; *A.*, 1915, i, 658.

[5] R. von Walther and R. Hübner, *J. pr. Chem.*, 1916, [ii], **93**, 119; *A.*, i, 559.

[6] D. A. Clibbens and M. Nierenstein, *T.*, 1915, **107**, 1491; *A.*, 1915, i. 1062.

[7] *Ann. Reports*, 1915, 89.

(? 72·25 per cent.), and into the ortho-position to the fluorine atom to the extent of 27·75 per cent.[8]

Reduction.—It is well known that the reduction of nitrobenzene to aniline is carried out technically by means of iron and only 1/40th of the amount of hydrochloric acid required by the following equation:

$$Ph{\cdot}NO_2 + 6HCl + 3Fe = Ph{\cdot}NH_2 + 3FeCl_2 + 2H_2O.$$

Many theories have been advanced to explain why the reaction proceeds after the iron has consumed the small amount of hydrochloric acid present, and various sets of equations have been formulated to represent the reduction as the result of a cycle of operations. P. N. Raikow[9] has recently reviewed these explanations and examined a fundamental equation in each experimentally. In Roscoe and Schorlemmer's view,[10] the initial reaction is followed by the reduction of nitrobenzene by means of ferrous chloride and hydrochloric acid:

$$Ph{\cdot}NO_2 + 6FeCl_2 + 6HCl = Ph{\cdot}NH_2 + 3Fe_2Cl_6 + 2H_2O,$$

but reduction in this way cannot be realised experimentally.

O. N. Witt,[11] who worked with α-nitronaphthalene, represented the second stage of the cycle as the reduction of the nitro-compound by means of aqueous ferrous chloride:

$$R{\cdot}NO_2 + 6FeCl_2 + H_2O = R{\cdot}NH_2 + 3Fe_2Cl_4O.$$

This representation was criticised by A. Wohl[12] on two grounds, namely, (1) that, since nitrobenzene can be reduced by means of iron and aqueous calcium chloride, ferrous chloride is not essential, and (2) that nitrobenzene is not reduced by aqueous ferrous chloride at the concentration employed technically. Raikow also confirms the last result.

Wohl put forward another explanation which has been accepted by many writers of text-books. It is supposed that in the presence of ferrous chloride moist iron reduces nitrobenzene direct with the formation of ferric hydroxide:

$$Ph{\cdot}NO_2 + 2Fe + 4H_2O = Ph{\cdot}NH_2 + 2Fe(OH)_3,$$

and the latter then combines with ferric chloride to form a complex basic salt. Objection has been taken to this explanation on the ground that the halogen is thus gradually withdrawn from solution, when, in consequence, the vigour of the reaction should diminish, whereas this is not the case. To avoid this objection,

[8] F. Swarts, *Rec. trav. chim.*, 1915, **35**, 131; *A.*, i, 133.
[9] *Zeitsch. angew. Chem.*, 1916, **29**, i, 196, 239; *A.*, i, 469, 599.
[10] "Treatise on Chemistry," 1891, Vol. III, Pt. 3, p. 223.
[11] *Ding. polyt. J.*, 1887, **265**, 225; *A.*, 1887, 1048.
[12] *Ber.*, 1894, **27**, 1432, 1815; *A.*, 1894, i, 409, 450.

V. Meyer and, later, Béhal suggested modifications of Wohl's explanation, in which purely "catalytic" action is ascribed to the ferrous chloride.

A more satisfactory explanation is that given in Muspratt's book,[13] namely, that the aniline and ferrous chloride formed in the first stage of the reaction interact to give ferrous hydroxide and aniline hydrochloride, the latter then reacting with metallic iron to liberate hydrogen or effect reduction:

$$2Ph{\cdot}NH_2 + FeCl_2 + 2H_2O = 2Ph{\cdot}NH_2,HCl + Fe(OH)_2,$$
$$2Ph{\cdot}NH_2,HCl + Fe = 2Ph{\cdot}NH_2 + FeCl_2 + H_2.$$

Both these reactions can be confirmed experimentally, but a more fundamental explanation of the process is put forward by Raikow. He attributes the continuation of the reduction primarily to hydrolytic dissociation of the ferrous chloride. The hydrochloric acid so formed then reacts with metallic iron to liberate hydrogen or effect reduction of nitrobenzene, regenerating ferrous chloride. The reaction may then be represented as follows:

$$Ph{\cdot}NO_2 + 3Fe + 6HCl = Ph{\cdot}NH_2 + 3FeCl_2 + 2H_2O.$$
$$3FeCl_2 + 6H_2O = [3Fe(OH)_2 + 6HCl].$$
$$[3Fe(OH)_2 + 6HCl] + 3Fe + Ph{\cdot}NO_2 =$$
$$3Fe(OH)_2 + 3FeCl_2 + 2H_2O + Ph{\cdot}NH_2.$$

This explanation closely resembles the one put forward to explain the reduction of nitrobenzene by iron and small quantities of acetic acid.[14]

Catalytic Reduction.—When aromatic alcohols, aldehydes, and ketones are reduced catalytically in acetic acid solution in the presence of colloidal platinum, they tend to yield hydrocarbons. Thus benzaldehyde yields toluene and methyl*cyclo*hexane; and benzophenone gives diphenylmethane and di*cyclo*hexylmethane. If, however, the alcoholic, aldehydic, or ketonic grouping is suitably protected, the hexahydro-derivative of the oxygenated substance may be obtained. For example, if benzylideneaniline is first reduced to benzylaniline by sodium and alcohol, and then submitted to the above catalytic process, dodecahydrobenzylaniline is obtained; and this, by oxidation to dodecahydrobenzylideneaniline and subsequent hydrolysis, yields hexahydrobenzaldehyde. Similarly, although phenylacetaldehyde yields *β-cyclo*hexylethyl alcohol, together with some ethylbenzene and ethyl*cyclo*hexane, on catalytic reduction, a better yield of the alcohol may be obtained by reducing the acetyl derivative of the aldehyde, phenylvinyl acetate, Ph·CH:CH·OAc. In the case of cinnamaldehyde, the reduction leads first to γ-phenyl-

[13] "Technisch-chemisches Handbuch," 1888, I, 942.

[14] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," 1910, p. 46.

propaldehyde, then to γ-phenylpropyl alcohol, and eventually to γ-*cyclo*hexylpropyl alcohol, with small quantities of propylbenzene and propyl*cyclo*hexane.[15]

Experiments have been carried out on the catalytic hydrogenation of organic compounds with non-noble metals at normal temperature and pressure. Good results have been obtained in aqueous-alcoholic solution, using, as catalyst, nickel precipitated as basic carbonate on to infusorial earth or other supporting substance, and reduced at 450°.[16]

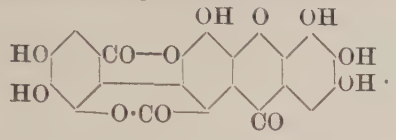
Catalytic reduction has been applied to the estimation of halogen in organic compounds, from which in many cases the halogen is quantitatively eliminated by treatment with hydrogen in the presence of palladinised calcium carbonate. A long list of substances which behave in this way is given; instances are, carbon tetrachloride, iodoform, trichloroacetic acid, chlorobenzene, *p*-dibromobenzene, and *m*-bromobenzoic acid.[17]

Oxidation.—The study of the oxidation of phenols, to which reference was made last year,[18] has been continued. Phenol itself yields, on electrochemical oxidation, quinol, benzoquinone, catechol, 4:4′-diphenol, 2:4′-diphenol, and *o*-hydroxydiphenyl ether. It is probable that the diphenols are intermediate products in the formation of benzoquinone and dihydroxybenzenes, since they yield these substances on electrochemical oxidation.[19] Derivatives of 1:2:3:4-tetrahydroxybenzene have been prepared by the oxidation of derivatives of pyrogallol containing a free hydroxyl group; for instance, 2-hydroxy-3:4-dimethoxyacetophenone yields 2:5-dihydroxy-3:4-dimethoxyacetophenone on treatment with persulphates in alkaline solution.[20] In view of the fact, previously known, that salicylaldehyde yields gentisaldehyde (2:5-dihydroxybenzaldehyde) on oxidation with persulphates, a knowledge of the behaviour of its alkyl ethers and closely related compounds is of interest. It has now been found that anisaldehyde yields anisic acid when oxidised in this way, whilst vanillin yields the diphenyl derivative dehydrodivanillin. The latter may be obtained in excellent yield by the use of sodium persulphate in the presence of a little ferrous sulphate.[21]

By the oxidation of gallic acid with arsenic acid in sulphuric acid

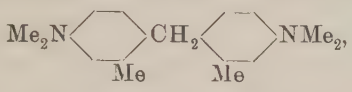
[15] A. Skita, *Ber.*, 1915, **48**, 1685; *A.*, i, 41.
[16] C. Kelber, *ibid.*, 1916, **49**, 55; *A.*, ii, 309.
[17] M. Busch and H. Stöve, *ibid.*, 1916, **49**, 1063; *A.*, ii, 534.
[18] *Ann. Reports*, 1915, 94.
[19] F. Fichter and E. Brunner, *Bull. Soc. chim.*, 1916, [iv], **19**, 281; *A.*, i, 644.
[20] G. Bargellini, *Gazzetta*, 1916, **46**, i, 249; *A.*, i, 489.
[21] K. Elbs and H. Lerch, *J. pr. Chem.*, 1916, [ii], **93**, 1; *A.*, i, 315.

solution, a new colouring matter, flavogallol, has been obtained. The investigation of this interesting substance has not yet been completed, but the following formula is tentatively proposed [22]:

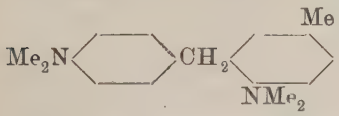


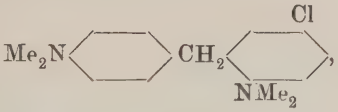
Steric and other Influences of Substituent Radicles.

The influence of different ortho-substituents on the readiness with which diphenylmethane derivatives are oxidised to the corresponding benzhydrols by means of lead peroxide has been studied.[23] In 4:4′-tetramethyldiamino-2:2′-dimethyldiphenylmethane,

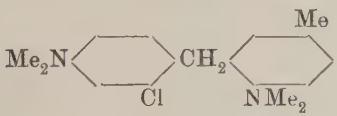


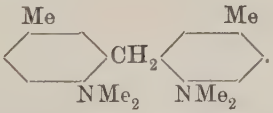
the methyl groups only permit the formation of the hydrol to a very small extent, but their replacement by chlorine greatly diminishes the steric hindrance. The influence of one or more dimethylamino-groups in the ortho-position has now been examined, and it is found that the two following compounds undergo oxidation to the corresponding hydrols:





whilst the two formulated below do not:





Another investigation deals with the cleavage of benzhydrols. It was shown some years ago that *p*-aminobenzhydrol and its derivatives react with bromine in a manner exemplified as follows [24]:

$$OH\cdot CHPh\cdot C_6H_2Br_2\cdot NH_2 + Br_2 = Ph\cdot CHO + C_6H_2Br_3\cdot NH_2 + HBr.$$

It is now found that not only bromine, but also other reagents, such as nitric acid and nitrous acid, capable of effecting substitution in the benzene nucleus, bring about a similar cleavage. A number of benzhydrols with a para-substituent have been examined,

[22] A. G. Perkin, *T.*, 1916, **109**, 529; *A.*, i, 485.

[23] J. von Braun, *Ber.*, 1916, **49**, 691; *A.*, i, 473.

[24] L. Clarke and G. J. Esselen, jun., *J. Amer. Chem. Soc.*, 1911, **33**, 1135; 1914, **36**, 308; *A.*, 1911, i, 725 1914, i, 278.

and it is found that the readiness with which they undergo cleavage corresponds with the efficiency of the para-substituent in promoting substitution in the benzene nucleus, the substituents examined being effective in the following order:

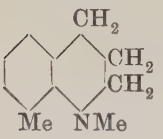
$$Me_2N > OH > OMe > Me > Br.$$

Further substituents in the ortho-position to these groups invariably diminish the relative amount of cleavage, and, with all but the most effective, diortho-substitution stops it altogether.[25]

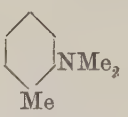
The readiness with which ortho-substituted derivatives of dimethylaminobenzene undergo different reactions has been compared.[26] The reactions studied were (1) the introduction of formaldehyde into the para-position, which yields dimethylaminobenzyl alcohols, (2) the power of forming malachite-green-like dyes on condensation with benzaldehyde and zinc chloride and subsequent oxidation, (3) the addition of methyl iodide, and (4) the oxidation of the dimethylaminobenzyl alcohols by means of formaldehyde to the corresponding benzoic acids. The four reactions were studied with *o*-methyl-, *o*-chloro-, *o*-bromo-, and *o*-methoxy-dimethylaminobenzene under identical conditions, and the following comparative results were obtained:

Ortho-substituent	Me.	Cl.	Br.	OMe.
Reaction 1	6	36	45	60 per cent.
2	Negative.	Negative.	Trace.	Positive.
3	7·6	15·6	16%	∞
4	5	16	36	36 per cent.

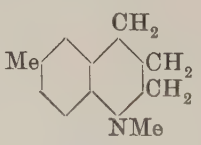
It was found, further, that the 1:8- and 1:6-dimethyl-1:2:3:4-tetrahydroquinolines (I and II) were much more reactive than *o*- and *p*-dimethylaminotoluenes (I*a* and II*a*) respectively:



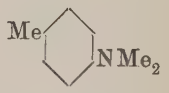
(I.)



(I*a*.)



(II.)



(II*a*.)

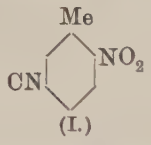
An interesting study of the relative quantities of ortho- and para-nitrophenyl esters obtained by the nitration of different phenyl esters has been carried out. The amounts of the *o*-nitrophenyl ester were as follows: with triphenyl phosphate, 5·6; diphenyl phosphate, 16·0; phenyl phosphate, 16·3; phenyl carbonate, 10·7; and phenyl methyl carbonate, 14·9 per cent. In the case of phenyl stearate, none of the *o*-nitrophenyl ester appeared to be formed,

[25] E. P. Kohler and R. H. Patch, *J. Amer. Chem. Soc.*, 1916, **38**, 1205; *A.*, i, 557.

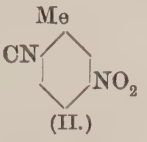
[26] J. von Braun, *Ber.*, 1916, **49**, 1101; *A.*, i, 647

whilst phenyl acetate gave 20—25 per cent. of the *o*-nitrophenyl ester contaminated with some of the 2:4-dinitrophenyl ester.[27]

The following is an example of the combined influence of certain groups in preventing the reaction of another group. Neither 6-nitro-*m*-toluonitrile (I)[28] nor 5-nitro-*o*-toluonitrile (II)[29] can be



(I.)



(II.)

reduced to the corresponding amino-nitrile. This is apparently due to the combined influence of the para-cyano-group and the alkyl group on the stability of the nitro-group, for the carboxylic acids on the one hand, and *p*-nitrobenzonitrile on the other, can be readily reduced. Incidentally, it may be of interest to note that the oxidation of 5-nitro-*o*-toluonitrile, which may be prepared from 5-nitro-*o*-toluidine by the Sandmeyer reaction, is a ready method for the preparation of 5-nitrophthalic acid.

Alkyl Ethers of Polyhydric Phenols.

A very large number of naturally occurring substances are derivatives of alkylated polyhydric phenols. Most of the alkaloids containing a quinoline or *iso*quinoline nucleus are substituted in the benzene portion of the molecule by hydroxy-, methoxy-, or methylenedioxy-groups. A knowledge of the properties of the corresponding benzene derivatives which are likely to be formed in the degradation of such substances is therefore of great importance in the determination of constitution. In his comprehensive investigation of cryptopine, W. H. Perkin, jun.,[30] has obtained a large number of degradation products of this type, many of which were previously unknown. In some cases the determination of the constitution of the degradation product has been a matter of considerable difficulty, as, for instance, in the case of the compound $C_9H_8O_3$. This had the odour of piperonal, and gave an oxime, semicarbazone, and phenylhydrazone, and, therefore, appeared to be a methyl derivative of piperonal, having the formula

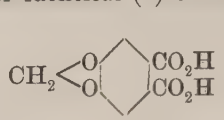
$$CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO.$$

On oxidation, it yielded a methylpiperonylic acid,

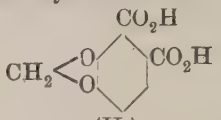
$$CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H,$$

[27] (Mlle.) J. M. A. Hoeflake, *Rec. trav. chim.*, 1916, **36**, 24; *A.*, i, 472.
[28] Beilstein and Kreusler, *Annalen*, 1867, **144**, 175.
[29] M. Mayer, *J. pr. Chem.*, 1915, [ii], **92**, 137; *A.*, 1915, i, 958.
[30] *T.*, 1916, **109**, 815.

but this could not be oxidised to the dicarboxylic acid, which would be either identical (I) or isomeric (II) with hydrastic acid:

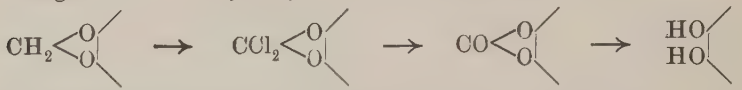


(I.)

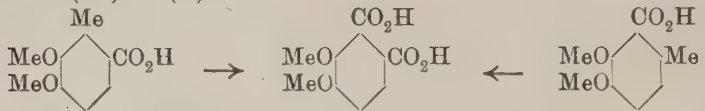


(II.)

The methylpiperonylic acid was therefore converted into the corresponding dimethoxymethylbenzoic acid by first forming dihydroxymethylbenzoic acid under the conditions recommended by G. Barger[31] for the hydrolysis of a methylenedioxy-group:

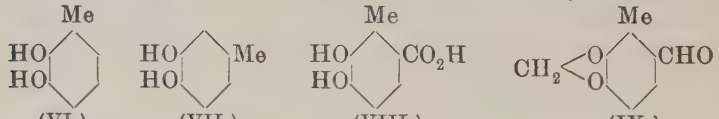


and subsequent methylation. This acid gave a good yield of hemipinic acid (III) on oxidation, and therefore had one of the two formulæ (IV) or (V):



(IV.) (III.) (V.)

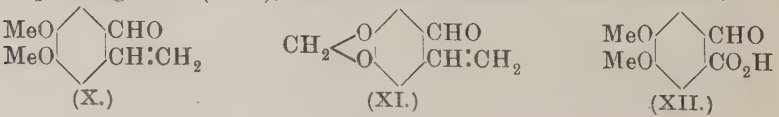
It was next found that the dihydroxymethylbenzoic acid was decomposed by heating with water at 170—180° with elimination of carbon dioxide and formation of a dihydroxytoluene. This proved to be *iso*homocatechol (VI), and not homocatechol (VII), and consequently the hydroxymethylbenzoic acid from which it was derived had the formula (VIII), and the methyl derivative of



(VI.) (VII.) (VIII.) (IX.)

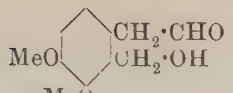
piperonal, of which the constitution was sought, had the formula (IX).

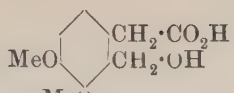
Other new derivatives of polyalkyloxybenzenes, described in this very interesting paper, include 4:5-dimethoxy-2-vinylbenzene (X), which is closely related to hydrastal (XI), and *m*-opianic acid (XII), both of which were obtained from cryptopine, and ω-hydroxy-3:4-dimethoxy-*o*-tolylacetaldehyde (XIII) with the corresponding acid (XIV), which were obtained from berberine.



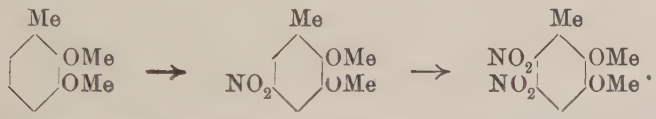
(X.) (XI.) (XII.)

[31] *T.*, 1908, **93**, 572

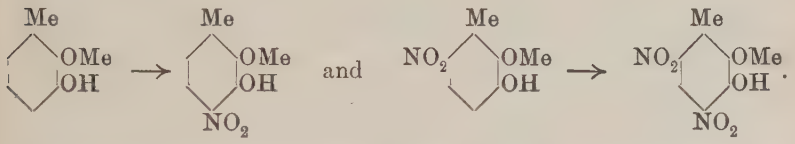

(XIII.)


(XIV.)

A knowledge of the nitro-derivatives of 2:3-dimethoxytoluene and 2:3-dimethoxybenzoic acid is of importance in connexion with two naturally occurring substances, the dyestuff santalin, and hydrourushiol (1-*n*-pentadecyl-2:3-dihydroxybenzene), a constituent of Japanese lac. 2:3-Dimethoxytoluene yields on nitration first 5-nitro-2:3-dimethoxytoluene, which gives 5-nitro-2:3-dimethoxybenzoic acid on oxidation, and then 5:6-dinitro-2:3-dimethoxytoluene:

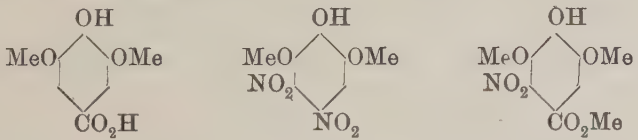


3-Hydroxy-2-methoxytoluene, however, yields first a mixture of the 4- and 6-mononitro-derivatives, and then 4:6-dinitro-3-hydroxy-2-methoxytoluene:



By the oxidation of the methyl ether of the 4-nitro-derivative the hitherto unknown 4-nitro-2:3-dimethoxybenzoic acid has been obtained. The proofs of the constitutions of the above substances are of considerable interest, and the original papers[32] should be consulted.

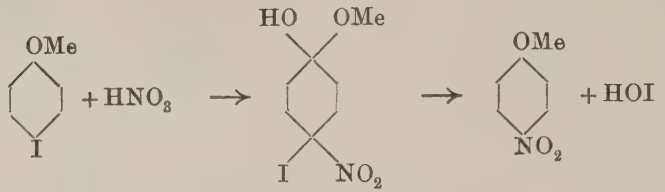
It may be noted that whilst syringic acid (I) in cold acetic acid solution yields 4:5-dinitropyrogallol 1:3-dimethyl ether (II) on nitration, its methyl ester yields in acetic anhydride at −5° methyl 2-nitrosyringate (III).[33]


(I.) (II.) (III.)

[32] R. Majima and Y. Okazaki, *Ber.*, 1916, **49**, 1482, and *Sci. Rep. Tôhoku Imp. Univ.*, 1916, **5**, 215; *A.*, i, 808; compare also J. C. Cain and J. L. Simonsen, *T.* 1914, **105**, 156.

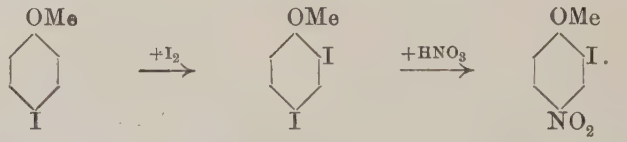
[33] M. T. Bogert and E. Plaut, *J. Amer. Chem. Soc.*, 1915, **37**, 2723; *A.*, i, 146.

F. Reverdin's[34] observation that *p*-iodoanisole yields on nitration *o*-iodo-*p*-nitroanisole, with apparent migration of the iodine atom, has led Mrs. G. M. Robinson[35] to study the mechanism of this reaction. She expresses the view that the reaction is not due to migration of the iodine atom, but depends on the liberation of iodine and its subsequent entry into the molecule in the ortho-position. *o*-Iodo-*p*-nitroanisole is doubtless formed to some extent as follows:



$$HOI + HI = I_2 + H_2O$$

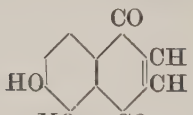
but the process mainly responsible for its formation is probably the following:



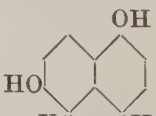
since di-iodoanisole can actually be isolated as an intermediate product of the reaction, and can be converted into *o*-iodo-*p*-nitroanisole by further treatment with nitric acid

Dynamic Isomerism.

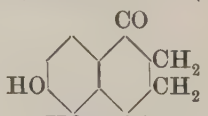
The discovery that the two isomeric hydrojuglones are keto-enol isomerides[36] has led to the investigation of the reduction product of naphthazarin (I), which easily gives a tetra-acetyl derivative, and is designated 1:4:5:6-tetrahydroxynaphthalene (II).



(I.)



(II.)



(III.)

[34] *Ber.*, 1896, 29, 1003; *A.*, 1896, i, 475.
[35] *T.*, 1916, **109**, 1078; *A.*, i, 805.
[36] *Ann. Reports*, 1915, 104.

It is now found[37] that this substance readily yields a phenylsemicarbazone and a phenylhydrazone, and there is some evidence of the formation of a diphenylsemicarbazone, but hydroxylamine and semicarbazide decompose it, owing to their alkalinity, so that derivatives of these reagents could not be prepared. 1:4:5:6-Tetrahydroxynaphthalene is therefore regarded as reacting according to the two formulæ II and III, and thus resembles phloroglucinol, which apparently exists only in one form, but exhibits both ketonic and phenolic properties.

Chromoisomerism.

Hypotheses designed to explain the existence of a substance in forms of more than one colour have been plentiful during recent years. Hantzsch, as is well known, depicts the differently coloured varieties as structural isomerides, the difference in structure depending either on the arrangement of the normal linkings or on the arrangement of the subsidiary valencies. In the case of helianthin and the aminoazobenzenes, an account of his views was given in a previous Report,[38] and these have since been elaborated by their author in further papers.[39]

Hantzsch[40] has now observed chromoisomerism in the case of compounds free from nitrogen, namely, in substances of the ethyl acetoacetate type. Symmetrical compounds of the general formula $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R$, for example, acetylacetone and indandiones, give monochromic salts only, but asymmetric compounds of the general formula $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R'$ give in many cases chromoisomeric salts, which may be formulated $R{\cdot}C(OM){:}CH{\cdot}CO{\cdot}R'$ and $R{\cdot}CO{\cdot}CH{:}C(OM)R'$ respectively (where M represents the metal); or, when the residual affinity between the metal and the unsaturated carbon atom is taken into account, they are given the conjugated formulæ

$$R{\cdot}\underset{\displaystyle O\text{—}M\cdots O}{\overset{\displaystyle \diagup\!\!\diagdown}{C}}{=}CH{-}\underset{\displaystyle \diagup\!\!\diagdown}{\overset{\displaystyle \diagup\!\!\diagdown}{C}}R' \qquad \text{and} \qquad R{\cdot}\underset{\displaystyle \diagup\!\!\diagdown}{\overset{\displaystyle \diagup\!\!\diagdown}{C}}{-}CH{=}\underset{\displaystyle O\cdots M\text{—}O}{\overset{\displaystyle \diagup\!\!\diagdown}{C}}R'.$$

Instances of the formation of chromoisomeric salts have been observed with ethyl succinylsuccinate, ethyl dihydroxybenzoquinonedicarboxylate, and ethyl 2:5-dihydroxyterephthalate, and in each case the chromoisomerism is attributed to the existence

[37] A. S. Wheeler and V. C. Edwards, *J. Amer. Chem. Soc.*, 1916, **38**, 387; *A.*, i, 392.

[38] *Ann. Reports*, 1913, 107.

[39] *Ber.*, 1915, **48**, 158, 167; *A.*, 1915, i, 321, 322.

[40] *Ibid.*, 785, 797; *A.*, 1915, i, 549, 551.

of the salt in two structurally isomeric forms, which may be represented as

Benzenoid or phenolic salt. Quinonoid or enolic salt.

In the case of ethyl dihydroxyterephthalate, not only do the salts exist in two chromoisomeric forms, but also the free ester, which occurs in a colourless and a yellow variety. The colourless form is optically similar to ethyl dimethoxyterephthalate, and must therefore be the true dihydroxy-ester, whilst the yellow form is assumed to have the quinonoid or enolic formula.

The same author puts forward a similar explanation of the chromoisomerism of certain salts of phenolic aldehydes, namely, that they are to be formulated as follows:

$$MO\cdot C_6H_4\cdot CHO \text{ and } O{:}C_6H_4{:}CH\cdot OM,$$

the paler-coloured salt having the phenolic and the darker-coloured salt the quinonoid–enolic formula. This suggestion has led to a controversy[41] with H. Pauly, who contests many of Hantzsch's statements and refers to the colour of the salts of substituted *m*-hydroxybenzaldehydes. These have only been observed in one form, but some colourless *m*-hydroxybenzaldehydes yield colourless salts, whilst others yield yellow salts. The existence of these yellow salts is held to refute Hantzsch's view that the deep colour of the salts of phenolic aldehydes is due to quinonoid structure, for there is an increasing volume of evidence against the existence of meta-quinonoids. Pauly contests Hantzsch's view that the chromoisomerism of phenolic aldehydes is due to desmotropy, preferring to regard the phenomenon in the light of the valence–electron theory.

That the occurrence of chromoisomerides may often be attributed simply to polymorphism has been pointed out previously[42] in these Reports, and this view is now supported by P. Pfeiffer,[43] who offers an ingenious speculation on the internal structure of certain chromoisomerides. He finds that nitromethoxystilbenes containing the methoxy-group in the para-position, and the nitro-group in the second benzene nucleus, as, for instance, 4-nitro-4′-methoxystilbene, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, occur in two forms, a yellow and an orange, one of which is usually stable at lower and the other at higher temperatures. Both forms have the same

[41] A. Hantzsch. *Ber.*, 815, 1332; 1916, **49**, 234; *A.*, 1915, i, 551, 1062; 1916, i, 403; H. Pauly, *ibid.*, 1915, **48**, 934, 2010; *A.*, 1915, i, 689; 1916, i, 150.

[42] *Ann. Reports*, 1911, 54–60; 1913, 252.

[43] *Ber.*, 1915, **48**, 1777; *A.*, i, 24.

melting point and give solutions identical in colour. The nitromethoxystilbenes give greenish-yellow solutions in benzene, but orange solutions in trichloroacetic acid, and, where crystalline additive products have been isolated, those with benzene and acetic acid are yellow, whilst those with substances having a higher degree of residual affinity, such as trichloroacetic acid and stannic chloride, are orange. The removal of the second component of such additive compounds is found to cause a change of colour; thus, the additive compound of 2-nitro-4-benzoylamino-4′-methoxystilbene and acetic acid is yellow, and on gentle heating loses acetic acid, leaving the orange variety of the stilbene, whilst the additive compound of the same stilbene and trichloroacetic acid is orange, and, on removal of the acid by the same means, yields the yellow variety of the stilbene.

In order to explain these results, Pfeiffer has recourse to his theory of halochromy,[44] and to the knowledge recently gained of crystal-structure by the researches of von Laue and the Braggs. The phenomenon of halochromy in the case of ketones depends on the co-ordinative addition of acids or metallic salts to the carbonyl–oxygen atoms of the ketone; this addition causes an alteration of energy in the ketone molecule, so that the carbonyl–carbon atom becomes more or less unsaturated, and therefore chromophoric in character. This is expressed as follows:

$$R_2C{:}O + HX \longrightarrow R_2C{:}O\ldots HX.$$
$$\downarrow$$

The coloured additive products of nitro-compounds with phenols or phenolic ethers, $R{\cdot}NO_2\ldots C_6H_5{\cdot}OH$, probably owe their colour to a similar cause. It is now suggested that the different coloured forms of the nitromethoxystilbenes are caused by the different arrangement of the single molecules in the crystals. Where the nitro-group of each stilbene molecule is combined co-ordinatively with the residual affinity of an unsaturated carbon atom of another molecule, coloured compounds, similar to the additive compounds of nitro-compounds and phenolic ethers, will be produced. Such compounds will have the darker, orange form. In the yellow form it is supposed that the arrangement of the single molecules is due to polymerisation similar to that occurring with nitroso-compounds. Very roughly, the idea may be represented as follows:

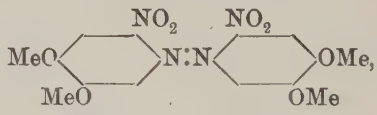
$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$	$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$
$MeO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$	$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$
Orange.	Yellow.

The curious colour reversal noted in the case of 2-nitro-4-benzoylamino-4′-methoxystilbene is then explained as follows. The orange-

[44] *Annalen*, 1911, **383**, 92; *A.*, 1911, i, 788.

coloured solution of the trichloroacetic acid compound contains the co-ordination compound $R{\cdot}NO_2{\ldots}HO{\cdot}CO{\cdot}CCl_3$, in which the residual affinity of the oxygen atom of the nitro-group is already saturated by the trichloroacetic acid molecule. There is, therefore, no tendency for this substance to crystallise in the form in which the nitro-group is co-ordinatively combined with an unsaturated carbon atom of another molecule of the stilbene. It is supposed to crystallise, therefore, according to the scheme of formation of the yellow crystals of the free stilbene, and the fact that the substance is actually orange in colour is due to the halochromic combination of the trichloroacetic acid molecule; on the removal of this, the yellow form of the free stilbene remains. The structure of the yellow acetic acid compound is such that the stilbene molecules which it contains are arranged as in the orange-coloured stilbene crystals, but the acetic acid molecules saturate more or less completely the free colour-causing affinities and give rise to the paler (yellow) form; on the removal of the acetic acid, the orange form of the free stilbene crystals appears.

It is perhaps of interest in connexion with Pfeiffer's work to note the existence of 2:2′-dinitro-4:5:4′:5′-tetramethoxyazobenzene,



in two varieties, forming red and yellow needles respectively. In this case, however, the separate colours are preserved after the two substances have been dissolved in sulphuric acid, recovered by dilution with water, and recrystallised, and it is thought that the anomalous colour of one of them is due to a small proportion of a probably isomorphous impurity.[45]

Another interesting suggestion as to the cause of chromoisomerism in a special case is put forward by I. Lifschütz and F. W. Jenner.[46] *p*-Nitrophenylacetonitrile forms two isomeric sodium salts, one of which gives a red alcoholic solution, and is the more stable to alkalis, whilst the other gives a green alcoholic solution, and is obtained by leaving the red solution for some time or treating it with carbon dioxide. The spectra of the red and green salts are identical in the ultra-violet and analogous in the visible region, and therefore the green salt, like the red,[47] must

[45] (Mrs.) G. M. Robinson and R. Robinson, *T.*, 1915, **107**, 1753; *A.*, i, 166.
[46] *Ber.*, 1915, **48**, 1730; *A.*, i, 45.
[47] Compare J. T. Hewitt, F. G. Pope and (Miss) W. I. Willett, *T.*, 1912, **101**, 1770.

have a quinonoid configuration. The authors indicate a difference between the two salts by representing them as stereoisomerides, thus:

preferring this explanation to one involving the residual affinities of the nitro- and cyano-groups in a 7- or 8-membered ring.

Triarylmethyl.

A number of interesting reactions of sodium triphenylmethyl have been described. This substance cannot be condensed with any compound capable of reacting in an enolic form, since the sodium atom is then replaced at once by hydrogen, but, subject to this limitation, it can be condensed with esters to yield ketones, and aldehydes to yield alcohols. Thus, methyl benzoate yields β-benzpinacolin,

$$Ph_3CNa + MeO{\cdot}COPh = Ph_3C{\cdot}COPh + MeONa,$$

formaldehyde gives triphenylethanol, $CPh_3{\cdot}CH_2{\cdot}OH$, and benzaldehyde tetraphenylethanol, $CPh_3{\cdot}CHPh{\cdot}OH$. The reactions of sodium triphenylmethyl are thus similar to those of Grignard's reagents. Sodium triphenylmethyl combines with sulphur dioxide to yield sodium triphenylmethylsulphinate, $CPh_3{\cdot}SO_2Na$, but does not react with carbon monoxide. With ammonia it yields triphenylmethane and sodamide.[48] It reacts with tetramethylammonium chloride to give triphenylmethyltetramethylammonium, an interesting compound in which the nitrogen atom is linked to five hydrocarbon radicles.[49]

$$CPh_3Na + ClNMe_4 = CPh_3{\cdot}NMe_4 + NaCl.$$

Polycyclic Aromatic Hydrocarbons.

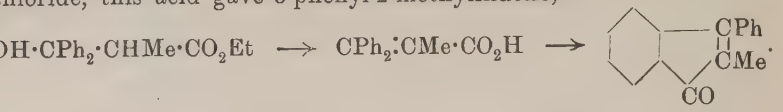
Indene.—A convenient method for the preparation of indones of a certain type has been described. It had previously been shown that the interaction of benzophenone, ethyl α-bromopropionate, and zinc led to the formation of ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate,

$$Ph_2CO + CHMeBr{\cdot}CO_2Et + Zn = ZnBr{\cdot}O{\cdot}CPh_2{\cdot}CHMe{\cdot}CO_2Et,$$
$$ZnBr{\cdot}O{\cdot}CPh_2{\cdot}CHMe{\cdot}CO_2Et + H_2O = ZnO + HBr + OH{\cdot}CPh_2{\cdot}CHMe{\cdot}CO_2Et,$$

which could be simultaneously hydrolysed and dehydrated to β-phenyl-α-methylcinnamic acid by treatment with diluted

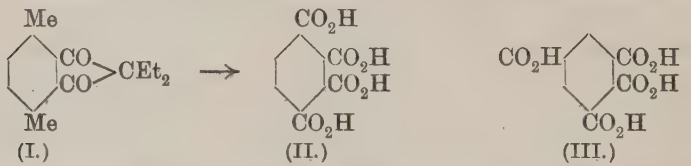
[48] W. Schlenk and R. Ochs, *Ber.*, 1916, **49**, 608; *A.*, i, 379.
[49] W. Schlenk and J. Holtz, *ibid.*, 603; *A.*, i, 385.

sulphuric acid in boiling acetic acid. Under the action of thionyl chloride, this acid gave 3-phenyl-2-methylindone,[50]



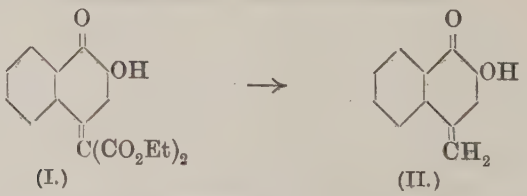
It is now found that ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate readily gives this indone in good yield when treated with cold concentrated sulphuric acid,[51] only the one operation being necessary. Similarly, ethyl β-hydroxy-ββ-diphenyl-α-ethylpropionate yields 3-phenyl-2-ethylindone.[52]

The method of synthesising indandiones by the condensation of diethylmalonyl chloride with aromatic compounds in the presence of aluminium chloride has proved useful in confirming the constitution of certain benzenetetracarboxylic acids. The condensation product with *p*-xylene, namely, 4 : 7-dimethyl-2 : 2-diethylindan-1 : 3-dione (I), gives mellophanic acid (II) on oxidation, whilst the condensation product with *m*-xylene gives prehnitic acid (III).[53]



These syntheses confirm the constitutions previously assigned to the acids.[54]

Naphthalene.—In connexion with the constitution of purpurogallin and lapachol, which yield naphthalene on distillation with zinc dust instead of 4-methylnaphthalene, as might be expected from the formulæ assigned to them, the study of a synthetic compound of similar type is of interest. 2-Hydroxy-1-keto-4-methylene-1 : 4-dihydronaphthalene (II), which was prepared by the action of



[50] H. Rupe, H. Steiger, and F. Fiedler, *Ber.*, 1914, **47**, 63 ; *A.*, 1914, i, 281.

[51] R. de Fazi, *Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 343 ; *A.*, i, 151.

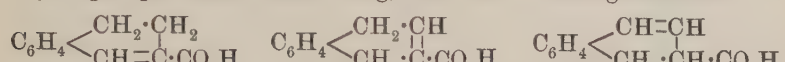
[52] R. de Fazi, *ibid.*, 1915, [v], **24**, ii, 150 ; *Gazzetta*, 1915, **45**, ii, 143 ; *A.*, 1915, i, 1063.

[53] M. Freund and K. Fleischer, *Annalen*, 1916, **441**, 14 ; *A.*, i, 317.

[54] A. Baeyer, *ibid.*, 1873, **166**, 325 ; *A.*, 1873, 755 ; H. Bamford and J. L. Simonsen, *T.*, 1910, **97**, 1908.

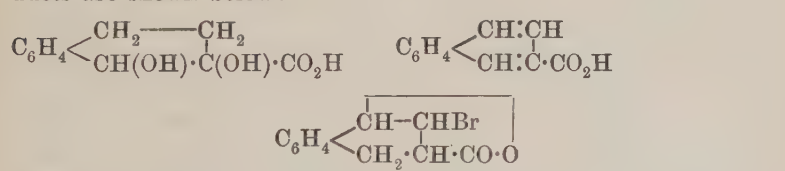
pyridine on 2-hydroxy-1-keto-4-dicarbethoxymethylene-1 : 4-dihydronaphthalene (I), also yields naphthalene when distilled with zinc dust, the methylene group being eliminated.[55] This result serves to remove a possible objection to the formulæ proposed for the natural compounds of, as yet, uncertain constitution.

The three possible dihydro-β-naphthoic acids, having the carboxylic group in the reduced ring, have the following formulæ:



(Δ^1.) (Δ^2.) (Δ^3.)

Two of these are obtained by the reduction of β-naphthoic acid with sodium amalgam, namely, a labile acid which is capable of resolution into optically active components, and is therefore the Δ^3 acid, and a stable acid, for which the Δ^2 formula has been proposed. It has now been found that both acids can be converted into a third isomeride by means of aqueous barium hydroxide at 160—180°. The dibromides of the three acids have been prepared and decomposed by means of cold 10 per cent. aqueous sodium carbonate; under these conditions, the new acid yields a dihydroxy-acid, the so-called stable acid yields β-naphthoic acid, whilst the labile acid yields a monobromolactone. The formulæ of these products are shown below:



The results leave no doubt as to the constitutions of the three dihydro-β-naphthoic acids. Confirmation of the Δ^1 formula for the new acid has been obtained by oxidising it to *o*-carboxyphenylpropionic acid.[56]

Similar work on the two known dihydro-α-naphthoic acids has been published.[57]

Anthracene.—Some interesting work has been carried out in connexion with the constitution of kermesic and carminic acids, the colouring principles of kermes dye and cochineal respectively.

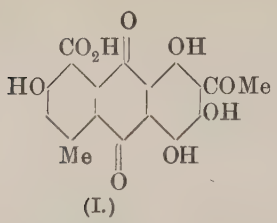
Previous work[58] has shown that kermesic acid has one of the following formulæ:

[55] H. F. Dean and M. Nierenstein, *T.*, 1916, **109**, 593; *A.*, i, 555.

[56] C. G. Derick and O. Kamm, *J. Amer. Chem. Soc.*, 1916, **38**, 400; *A.*, i, 394.

[57] O. Kamm and H. B. McClugage, *ibid.*, 419; *A.*, i, 395.

[58] *Ann. Reports*, 1913, 122.



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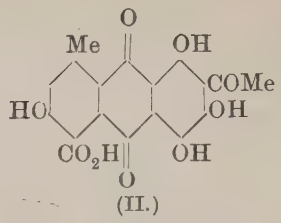
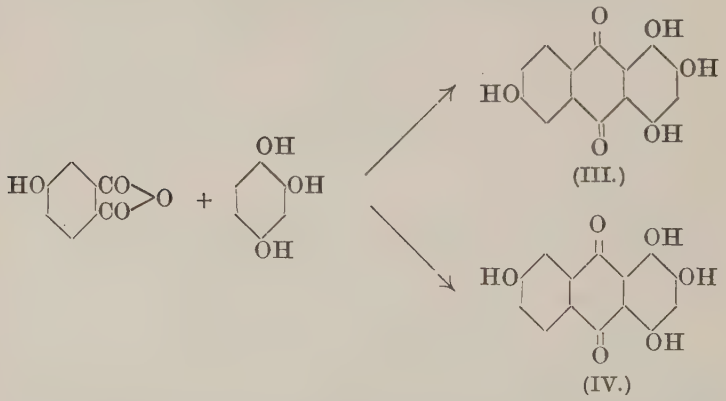


(II.)

and experiments are now recorded of which the double object was a preliminary study of syntheses in this field and an attempt to decide which of the above formulæ was correct. It is shown that purpurin (1 : 2 : 4-trihydroxyanthraquinone) may be synthesised by the condensation of phthalic anhydride and hydroxyquinol (in the form of its triacetate). Similarly, 4-hydroxyphthalic anhydride yields with hydroxyquinol a tetrahydroxyanthraquinone, which might be either the 1 : 2 : 4 : 6-derivative, hydroxyflavopurpurin (III), or the 1 : 2 : 4 : 7-derivative, hydroxyanthrapurpurin (IV) :



(III.)

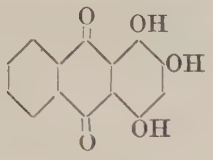
(IV.)

The product proves to be the former substance, for it is identical with the oxidation product of flavopurpurin, 1 : 2 : 6-trihydroxyanthraquinone. Since kermesic acid closely resembles hydroxyanthrapurpurin (IV) (obtained by the oxidation of anthrapurpurin) in its absorption spectrum and tinctorial properties, whilst it differs from hydroxyflavopurpurin in these respects, it is concluded that formula I correctly represents the relative positions of the hydroxyl groups in kermesic acid.[59]

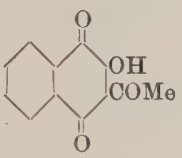
Carminic acid appears to be closely related to kermesic acid, but of more complex constitution. Amongst its properties, the capacity of yielding, by degradation, derivatives of naphthaquinone is peculiar, and experiments have now been made to determine whether purpurin (V), which it resembles in tinctorial

[59] O. Dimroth and R. Fick, *Annalen*, 1916, **411**, 315 ; *A.*, i, 561.

properties, can be made to undergo a similar degradation. These have given an affirmative result, for purpurin yields 2-hydroxy-3-acetyl-α-naphthaquinone (VI) when oxidised with alkaline hydrogen peroxide in the presence of cobalt oxide.[60]



(V.)



(VI.)

Phenanthrene.—An ortho-hydroxyaldehyde has been prepared from 3-phenanthrol by Gattermann's method. Of the two possible

(VII.)

(VIII.)

formulæ for this substance, VII and VIII, the first has now been established by converting the substance into morphol (3 : 4-dihydroxyphenanthrene).[61]

Hydrocyclic Compounds and Terpenes.

By the action of zinc dust on the compound $C(CH_2Br)_4$ in aqueous-alcoholic solution, G. Gustavson[62] obtained a hydrocarbon which he regarded as vinyltrimethylene (I). Addition and subsequent elimination of hydrogen iodide transformed it into an isomeride, which was represented as ethylidenetrimethylene (II).

$CH_2{:}CH{\cdot}CH{<}\begin{matrix}CH_2\\CH_2\end{matrix}$ (I.) $\qquad$ $CH_3{\cdot}CH{:}C{<}\begin{matrix}CH_2\\CH_2\end{matrix}$ (II.)

These compounds have since been the subject of several investigations, which left their constitution doubtful, but O. Philipov[63] has now shown that they are methylene*cyclo*butane and methyl*cyclo*butene respectively.

$CH_2{:}C{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH_2$ $\qquad$ $CMe{<}\begin{matrix}CH\\CH_2\end{matrix}{>}CH_2$.

[60] O. Dimroth and E. Schultze, *Annalen*, 1916, **411**, 339; *A.*, i, 563.

[61] J. W. Smith, *T.*, 1916, **109**, 568; *A.*, i, 487.

[62] *J. pr. Chem.*, 1896, [ii], **54**, 98, 105; with Miss H. Bulatoff, *ibid.*, 1897, [ii], **56**, 93; *A.*, 1896, i, 669; 1898, i, 13.

[63] *Ibid.*, 1916, [ii], **93**, 162; *A.*, i, 551. Compare also N. J. Demjanov, *Ber.*, 1908, **41**, 915; *A.*, 1908, i, 329, and A. Favorski and W. Batalin, *ibid.*, 1914, **47**, 1648; *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 726; *A.*, 1914 i, 815; 1915, i, 390.

The evidence supporting this view is based on the results of the oxidation and reduction of these compounds. On oxidation, methylene*cyclo*butane gives *cyclo*butanone, together with a mixture of acids, including glutaric acid, the unexpected formation of which he explains by the following scheme:

$$CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C{:}CH_2 \longrightarrow CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C(OH)\cdot CH_2\cdot OH \longrightarrow$$

$$CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C(OH)\cdot CHO \longrightarrow CH_2\langle\begin{matrix}CH_2\cdot CO\\CH_2\cdot CH\cdot OH\end{matrix} \longrightarrow$$

$$CH_2\langle\begin{matrix}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}.$$

Oxidation of methyl*cyclo*butene leads to lævulic and succinic acids, as follows:

$$CH_2\langle\begin{matrix}CMe\\CH_2\end{matrix}\rangle CH \longrightarrow CH_2\langle\begin{matrix}CMe(OH)\\CH_2\end{matrix}\rangle CH\cdot OH \longrightarrow$$

$$COMe\cdot CH_2\cdot CH_2\cdot CO_2H \longrightarrow C_2H_4(CO_2H)_2.$$

An identical reduction product was obtained from the two hydrocarbons, and this has been identified as methyl*cyclo*butane by comparison with a specimen of this substance prepared synthetically by Kishner's method, as indicated below:

$$CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle CH\cdot CHO \longrightarrow CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle CH\cdot CH{:}N\cdot NH_2 \longrightarrow$$

$$CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle CHMe.$$

N. Kishner,[64] in a further study of his method of forming hydrocyclic compounds, shows that 5-phenyl-3-styrylpyrazoline (I), obtained by the action of hydrazine on distyryl ketone, cannot be converted into a derivative of *cyclo*propane, but yields, on heating, 3:4-diphenyl*cyclo*pentane (II).

$$CHPh{:}CH\cdot C\langle\begin{matrix}CH_2\cdot CHPh\\N{-}{-}NH\end{matrix} \longrightarrow \begin{matrix}CHPh\cdot CH_2\\CHPh{-}{-}CH\end{matrix}\rangle CH$$

(I.) (II.)

The closely allied pyrazoline (III), however, when heated in the presence of potassium hydroxide and platinised porous tile, loses nitrogen, forming 1-phenyl-2-β-phenylethyl*cyclo*propane (IV).

$$CH_2Ph\cdot CH_2\cdot C\langle\begin{matrix}CH_2\cdot CHPh\\N{-}{-}NH\end{matrix} \longrightarrow CH_2Ph\cdot CH_2\cdot CH\langle\begin{matrix}CH_2\\CHPh\end{matrix}$$

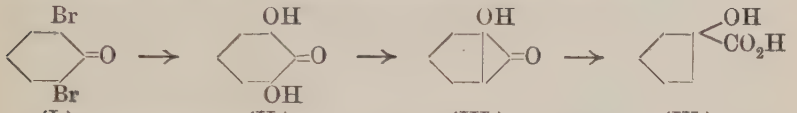
(III.) (IV.)

A method for the conversion of *cyclo*hexanones into *cyclo*pentanones has been elaborated, and many examples of its use have been described.[65] As an example, its application to *cyclo*-

[64] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1819; *A.*, i, 290.

[65] O. Wallach, M. Gerhardt, and W. Jessen, *Nachr. K. Ges. Wiss. Göttingen*, 1915, 244; *A.*, i, 487.

hexanone itself may be recorded. On bromination in acetic acid solution, this ketone yields a dibromide, which yields a ketone, $C_6H_8O_2$, and a hydroxycarboxylic acid, $C_6H_{10}O_3$, on treatment with dilute aqueous potassium hydroxide at the ordinary temperature. The hydroxy-acid decomposes into *cyclo*pentanone and carbon dioxide when distilled with lead peroxide and sulphuric acid, and therefore has the formula IV. The ketone, $C_6H_8O_2$, is represented by the formula III, and is probably formed by dehydration of the hypothetical intermediate product (II).



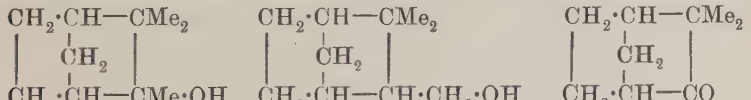
(I.) (II.) (III.) (IV.)

Camphene.—Now that the constitution of camphenic acid (I) been established by P. Lipp's synthesis,[66] probable formulæ can be assigned to some of its derivatives. On dry distillation the acid yields camphenonic acid, a ketonic acid, which, since it can be reconverted into camphenic acid by fusion with potassium hydroxide or treatment with sodium and alcohol, is represented by formula II.

(I.) (II.)

The *d*- and *l*-forms of camphenonic acid have also been obtained, in each case together with the *dl*-variety, from the camphenic acids derived from camphenes of strong dextro- and lævo-rotatory power respectively.[67]

Camphene hydrate, which is readily obtainable by the action of dilute alkali on camphene hydrochloride, can be reconverted, by gentle dehydration, into camphene having the original specific rotatory power. The hydrate is therefore formed without causing a change in the camphene skeleton. Of the two formulæ, I and II, which might represent it, the second is eliminated by the further evidence that camphene hydrate and its hydrochloride



(I.) (II.) (III.)

[66] *Ann. Reports.*, 1914, 119.

[67] O. Aschan, *Annalen*, 1915, **410**, 240; *A.*, i, 52.

show the typical behaviour of tertiary alcohol and chloride respectively.

Camphene hydrate, therefore, has the formula I, which also represents methylcamphenilol, a substance obtained by the action of magnesium methyl iodide on camphenilone (III).[68] The two compounds, camphene hydrate and methylcamphenilol, are not, however, identical, but must be regarded as stereoisomerides forming a pair comparable with borneol and *iso*borneol. Both compounds yield camphene on dehydration.[69]

The previously known chloride of hydroxymethylenecamphor may be prepared readily by the action of thionyl chloride on hydroxymethylenecamphor. When the chloride is treated with Grignard's reagents, the chlorine atom is replaced by an alkyl or aryl group.

$$C_8H_{14}\begin{cases}C{:}CHCl\\ CO\end{cases} + MgRX \longrightarrow C_8H_{14}\begin{cases}C{:}CHR\\ CO\end{cases}.$$

The constitution of the products obtained follows from the facts (1) that the phenylmethylenecamphor so produced is identical with the previously known benzylidenecamphor resulting from the action of benzaldehyde on sodium camphor, and (2) that the products yield with ozone some camphorquinone besides camphoric acid.[70]

Amongst other investigations of hydroaromatic compounds, attention may be directed to the following: an attempt to correlate the constitution and the physical properties of isomeric and homologous hydroaromatic compounds, referring mainly to *cyclo*hexane, *cyclo*hexene, *cyclo*hexanol, and *cyclo*hexanone and their methyl derivatives;[71] investigation of the constitutions of the four saturated bicyclic hydrocarbons, $C_{10}H_{18}$, to which the name fenchane has been given;[72] and a research on the synthesis of terpineols and terpins.[73]

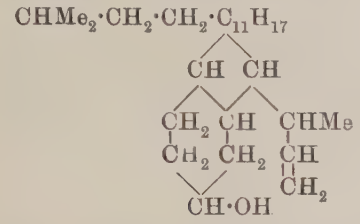
Cholesterol.

The earlier work on cholesterol was fully reviewed by A. Windaus[74] in 1908, and his work on the subject has since been dealt with in the Annual Report for 1912.[75] In the meantime,

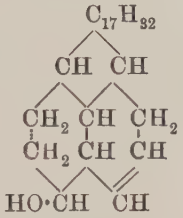
[68] S. Moycho and F. Zienkowski, *Ber.*, 1905, **38**, 2461; *A.*, 1905, i, 654.
[69] O. Aschan, *Annalen*, 1915, **410**, 222; *A.*, i, 51.
[70] H. Rupe and M. Iselin, *Ber.*, 1916, **49**, 25; *A.*, i, 409.
[71] K. von Auwers, *Annalen*, 1915, **410**, 287; *A.*, i, 130.
[72] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1590; *A.*, i, 269.
[73] O. Wallach and collaborators, *Nachr. K. Ges. Wiss. Göttingen*, 1915, 1; *A.*, i, 213.
[74] *Arch. Pharm.*, 1908, **246**, 117.
[75] Pp. 107, 109.

steady progress has been made in the study of the constitution of this complex substance.

The formula (I) favoured by Windaus at the later date has proved capable of explaining the more recently published developments of the work, but, in the latest paper by one of Windaus's pupils,[76] the modified formula (II) is put forward, for reasons which are to be given later.



(I.)



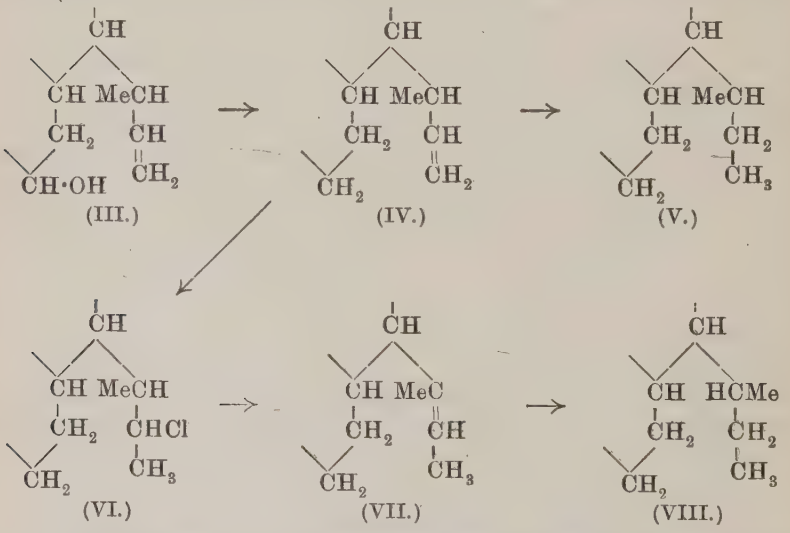
(II.)

The question as to whether cholesterol contains one or two double linkings seems now to be answered. The stability of the tetrabasic acid, $C_{21}H_{30}O_8$, prepared from cholesterol step by step,[77] makes it improbable that the latter contains more than one double linking.[78] Moreover, the molecular refractions of the substance and of many of its derivatives are in close agreement with those calculated on the assumption that only one double linking is present in the molecule of cholesterol.[79] The fact that it combines with six atoms of oxygen when treated with washed ozone of low concentration indicates that two double linkings are concerned in the reaction, but it seems probable, as C. Dorée[80] suggests, that only one double linking exists preformed in the cholesterol molecule, and that the secondary unsaturation is due to the opening up of a bridged ring under the action of ozone. This view has also been adopted by O. von Fürth and G. Felsenreich.[81]

During the last few years considerable progress has been made in determining the mutual relations of the reduction products of cholesterol. It has been shown that the supposed dihydrocholesterol, α-cholestanol, the product of the action of sodium and amyl alcohol, or of preformed sodium amyloxide, on cholesterol, is, in fact, an *iso*amyl derivative of cholesterol.[82] β-Cholestanol is doubtless the normal dihydro-derivative of cholesterol, for it can

[76] T. Westphalen, *Ber.*, 1915, **48**, 1064; *A.*, 1915, i, 884.
[77] A. Windaus, *ibid.*, 1908, **41**, 2566; *A.*, 1908, i, 728.
[78] Compare C. Dorée, *T.*, 1909, **95**, 653.
[79] L. A. Tschugaev and P. Koch, *Annalen*, 1911, **385**, 352; *A.*, 1912, i, 30.
[80] *Loc. cit.*; with L. Orange, *T.*, 1916, **109**, 46; *A.*, i, 261.
[81] *Biochem. Zeitsch.*, 1915, **69**, 416; *A.*, 1915, i, 679.
[82] A. Windaus and C. Uibrig, *Ber.*, 1913, **46**, 2487; *A.*, 1913, i, 969.

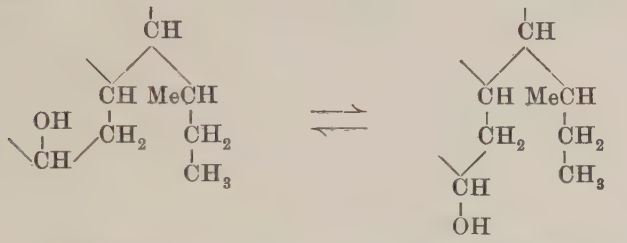
be prepared from the latter in nearly quantitative yield by reduction with hydrogen in the presence of platinum-black.[83] β-Cholestanol suffers partial rearrangement when heated with sodium amyloxide and amyl alcohol, yielding 10 per cent. of a stereoisomeride, termed ε-cholestanol, which can also be converted into the equilibrium mixture in the same way. Unlike β-cholestanol, ε-cholestanol is not precipitated by digitonin, and this property serves for the separation of the two isomerides. The isomerism of these alcohols is caused by the steric arrangement of the hydroxyl group and hydrogen atom about the asymmetric carbon atom to which they are attached, for both alcohols yield the same ketone on oxidation.[84] A similar relation has been shown to exist between coprosterol and ψ-coprosterol.[85] An important advance in our knowledge of the constitution of coprosterol is due to the discovery[86] that the saturated hydrocarbon, coprostane, derived from coprosterol, is identical with ψ-cholestane, which was prepared from cholesterol by J. Mauthner.[87] Windaus gives the following interpretation of the reactions carried out by Mauthner. Replacement of the hydroxyl group of cholesterol (III) by hydrogen gives cholestene (IV), which may be reduced to β-cholestane (V). The addition product (VI) of cholestene and hydrogen chloride gives chiefly the isomeric hydrocarbon,



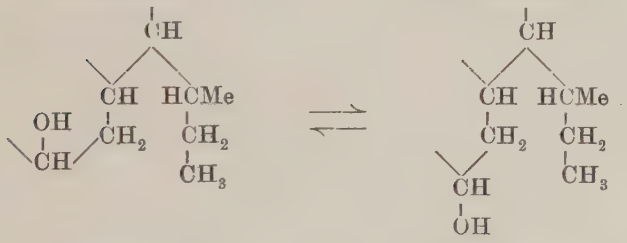
[83] R. Willstätter and E. W. Mayer, *Ber.*, 1908, **41**, 2199; *A.*, 1908, i, 636.
[84] A. Windaus and C. Uibrig, *ibid.*, 1914, **47**, 2384; *A.*, 1914, i, 1066.
[85] C. Dorée and J. A. Gardner, *T.*, 1908, **93**, 1630.
[86] A. Windaus and C. Uibrig, *Ber.*, 1915, **48**, 857; *A.*, 1915, i, 678.
[87] *Monatsh.*, 1909, **30**, 635; *A.*, 1909, i, 714.

ψ-cholestene (VII), on the removal of hydrogen chloride, and ψ-cholestene yields on reduction mainly ψ-cholestane (VIII).

In the conversion of cholestene (IV) into ψ-cholestene (VII), the asymmetric carbon atom to which the methyl group is attached loses its asymmetry, and on reduction of ψ-cholestene to ψ-cholestane (VIII), the asymmetry of this carbon atom is regained, when the formation of an isomeride is readily understood. It follows that β-cholestanol and coprosterol, the alcohols corresponding with the hydrocarbons β-cholestane and ψ-cholestane (coprostane), are similarly related. The relations of these two alcohols with ε-cholestanol and ψ-coprosterol may be represented as follows:

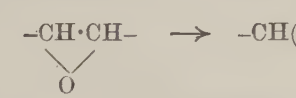


β-Cholestanol. ε-Cholestanol.



Coprosterol. ψ-Coprosterol.

The preparation of a structural isomeride of cholesterol, ψ-cholesterol, may be noted,[88] and also the formation of α-cholestantriol by the conversion of the ethylenic linking of cholesterol into an ethylene–oxide group, and subsequent hydrolysis.[89]



Cholesterylsulphuric acid, $C_{27}H_{45}\cdot O\cdot SO_3H$, has also been described.[90]

[88] A. Windaus and C. Resau, *Ber.*, 1915, **48**, 851; *A.*, 1915, i, 677.

[89] T. Westphalen, *ibid.*, 1064; *A.*, 1915, i, 884.

[90] J. A. Mandel and C. Neuberg, *Biochem. Zeitsch.*, 1915, **71**, 186; *A.*, 1915, i, 957.

Aromatic Compounds of Nitrogen.

The Constitution of Azoxy-compounds.—It was pointed out in 1902[91] (I) that our knowledge of the azoxy-compounds was very incomplete, and that the commonly accepted formula R·N—N·R (with O bridging the two nitrogens) lacked experimental foundation, for the known reactions of this class of compound could be explained equally well by the formula R·N:NO·R. Later work has brought to light properties of azoxy-compounds which can only be explained by the second formula, and has thus served to establish it. A. Angeli's discovery[92] that azobenzene gave azoxybenzene when oxidised with hydrogen peroxide in glacial acetic acid solution, was the first step leading to this result, for this method when applied to asymmetrically constituted azobenzenes gave rise to two isomeric azoxybenzenes, which were not interconvertible, and differed not only in their physical, but in their chemical properties—for example, their behaviour towards bromine and nitric acid. The following example will serve to illustrate the work which has been carried out on many pairs of isomerides.[93] Oxidation of *p*-bromoazobenzene with hydrogen peroxide in glacial acetic acid solution yields a mixture of *α*-*p*-bromoazoxybenzene, m. p. 73°, and *β*-*p*-bromoazoxybenzene, m. p. 92°. When treated with cold bromine, the *β*-isomeride yields 4:4′-dibromoazoxybenzene, whilst the *α*-compound is unacted on under these conditions,[94] but yields 2:4-dibromoazoxybenzene under the influence of bromine and iron at 115—120°.[95] This behaviour indicates the constitutional formulæ given below for the two isomerides, since it is probable that substitution takes place in the nucleus united to the tertiary nitrogen atom rather than in that united to the quinquevalent nitrogen atom.

(*α*) $C_6H_5\cdot NO{:}N\cdot C_6H_4Br \longrightarrow C_6H_5\cdot NO{:}N\cdot C_6H_3Br_2$.
(*β*) $C_6H_5\cdot N{:}NO\cdot C_6H_4Br \longrightarrow C_6H_4Br\cdot N{:}NO\cdot C_6H_4Br$.

The oxidation of azo- to azoxy-compounds is thus analogous to the oxidation of tertiary amines to their oxides, $R_3N \longrightarrow R_3N{:}O$.

The Constitution of Hydroxyazo-compounds.—Discussion of the constitution of hydroxyazo-compounds has been renewed with

[91] V. Meyer and P. Jacobsen, "Lehrb. d. organ. Chem.," 1902, II, i, 251.
[92] *Ann. Reports*, 1910, 98.
[93] Compare numerous papers by A. Angeli and B. Valori, 1910–1915.
[94] A. Angeli and B. Valori, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 155; *A.*, 1912, i, 321.
[95] B. Valori, *ibid.*, 1913, [v], **22**, ii, 125; *A.*, 1913, i, 1110.

reference to a particular case. Anthraquinone does not form a phenylhydrazone by the direct method, but a compound may be obtained by the action of phenylhydrazine on 9:9-dibromoanthrone:

$$NHPh\cdot NH_2 + CBr_2\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CO \longrightarrow NHPh\cdot N{:}C\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CO.$$

The same substance results from the action of benzenediazonium chloride on anthranol[96]:

$$N{:}NPhCl + CH\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\cdot OH \longrightarrow NPh{:}N\cdot C\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\cdot OH. \quad (A)$$

K. H. Meyer and K. Zahn[97] regard the compound as benzeneazoanthranol (*A*), basing their view on the following comparison of its properties with those of benzeneazoanthranyl benzoate,

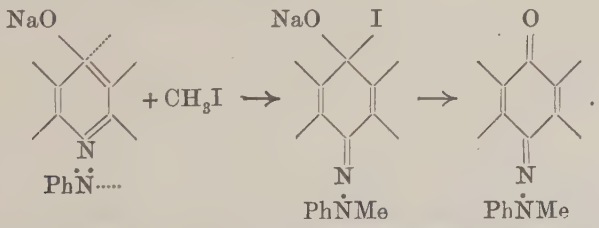
$$NPh{:}N\cdot C\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\cdot OBz \ (B),$$

and anthraquinonephenylbenzoylhydrazone,

$$NPhBz\cdot N{:}C\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CO \ (C):$$

	A.	*B.*	*C.*
Colour	red	dark red	yellow
Reaction with bromine	immediate	immediate	slow
Stability towards hydrolysis	great	great	small
Formation of halochromic additive products	positive	positive	negative

Whilst the *O*-benzoate was readily obtained by benzoylation of the parent substance, alkylation led to the formation of the *N*-substituted derivative, for example, anthraquinonephenylmethylhydrazone. Meyer and Zahn explain this difference in behaviour on the assumption that benzoylation is effected by a simple double decomposition, $R\cdot ONa + ClBz \longrightarrow R\cdot OBz$, whilst alkylation is the result of addition and subsequent fission, thus:



They do not, however, leave out of consideration the possibility that the compound is tautomeric in Laar's sense of the word, that is to say that it is a single substance with two possible formulæ, but

[96] F. Kaufler and W. Suchannek, *Ber.*, 1907, **40**, 518; *A.*, 1907, *i*, 225.
[97] *Annalen*, 1913, **396**, 152; *A.*, 1913, i, 537.

they reject this view in favour of representing the substance as benzeneazoanthranol.

G. Charrier has now attacked the constitution of this substance, and arrives at the opposite view, namely, that it is anthraquinone-phenylhydrazone. In order to follow his evidence on the subject, it is necessary, first of all, to refer briefly to the operation which he terms "diazo-scission." Hydroxyazo-compounds (or their ethers) combine with two molecules of nitric acid to form salts, which on heating undergo "diazo-scission," that is, conversion into a nitrophenol (or a nitrophenyl ether) and a diazonium nitrate[98]:

$$ArN{:}N{\cdot}C_6H_4{\cdot}OH + 2HNO_3 = NO_3{\cdot}NHAr{:}N{\cdot}C_6H_4{\cdot}OH_2{\cdot}NO_3 = NO_3{\cdot}NAr{:}N + OH{\cdot}C_6H_4{\cdot}NO_2 + H_2O.$$

Incidentally, it may be remarked that the dinitrates of aminoazo-compounds similarly yield, on fission, nitroarylamines and aryl-diazonium nitrates, a reaction which Charrier[99] represents as a decomposition of the dinitrate, whilst L. Casale[1] considers that the mechanism consists first of dissociation of the nitrate into the aminoazo-compound and nitric acid, followed by reaction between them. Charrier[2] finds that the diazo-scission characteristic of hydroxyazo-compounds fails completely in the case of the so-called benzeneazoanthranol. Moreover, the conditions for the hydrolysis of anthraquinonearylhydrazones are very similar to those of anthraquinonearylalkylhydrazones, which are known to have the hydrazone formula.[3] Taking into consideration the whole of the results described by the above authors, it appears to be probable that the compound in question really reacts in both the possible forms.

The Constitution of the Nitrosohydrazones.—When aldehyde-hydrazones are treated with nitrous acid or amyl nitrite, nitroso-derivatives are obtained, which can be rearranged by pyridine into azoaldoximes (III). For the nitroso-derivative, two formulæ are possible, representing the nitroso-group as attached to nitrogen (I) and carbon (II) respectively:

$$\begin{matrix} R{\cdot}N(NO){\cdot}N{:}CH{\cdot}R\ (I.) & \searrow & \\ & & R{\cdot}N{:}N{\cdot}CR{:}N{\cdot}OH\ (III.) \\ R{\cdot}NH{\cdot}N{:}CR{\cdot}NO\ (II.) & \nearrow & \end{matrix}$$

[98] Compare, for instance, G. Charrier and G. Ferreri, *Gazzetta*, 1914, **44**, i, 165; *A.*, 1914, i, 599.

[99] *Ibid.*, 1914, **44**, ii, 503; *A.*, 1915, i, 66.

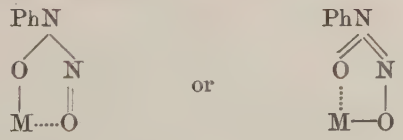
[1] *Ibid.*, 1915, **45**, ii, 397; *A.*, i, 225.

[2] *Atti R. Accad. Sci. Torino*, 1914–1915, **50**, 589; *Gazzetta*, 1915, **45**, i, 502; *A.*, 1915, i, 904.

[3] L. Omarini, *ibid.*, 1915, **45**, ii, 304; *A.*, i, 87. G. Charrier, *Atti R. Accad. Sci. Torino*, 1916, **51**, 572; *A.*, i, 511.

E. Bamberger and W. Pemsel[4] adopted the second formula for the nitroso-derivatives on various grounds, such as analogy to formazyl compounds and the nature of the decomposition products of the substances, but mainly because the nitroso-derivatives can be oxidised to nitroaldehydehydrazones, $R{\cdot}NH{\cdot}N{:}CR{\cdot}NO_2$, the nitro-group of which is undoubtedly united to a carbon atom. Moreover, whilst they were unable to prepare a nitroso-derivative of benzaldehydephenylmethylhydrazone, they succeeded in preparing a nitro-derivative, $PhMeN{\cdot}N{:}CPh{\cdot}NO_2$, of this compound. They considered and rejected as improbable the view that nitrosohydrazones had the formula (I), and were able to react in the dynamically isomeric form (II). M. Busch and H. Kunder[5] have raised this question again, and conclude that these nitroso-derivatives are true nitrosoamines. They find that whilst benzaldehydephenylhydrazone yields a nitroso-derivative when treated with a nitrite in acetic acid solution, benzaldehydephenylmethylhydrazone does not do so. Moreover, ketohydrazones also yield nitroso-compounds, which are in all essential particulars similar to the nitroso-aldehydehydrazones, and must be true nitroso-amines, $R{\cdot}N(NO){\cdot}N{:}CR_2$, since there is no alternative formula in this case. These facts indicate that the essential condition for the formation of a nitroso-derivative of this type is the presence of an imino-group, and that the presence of a hydrogen atom attached to the aldehydic carbon atom is unnecessary.

Complex Salts of Nitrosoarylhydroxylamines.—Nitrosophenylhydroxylamine, $PhN(NO){\cdot}OH$, forms with iron, copper, titanium, and zirconium internally complex salts, to which the following constitution has been attributed[6]:,



(where M is a univalent metal).

These salts are characterised by abnormal colour and ready solubility in organic solvents. Metals other than those mentioned above yield only normal salts of nitrosophenylhydroxylamine. O. Baudisch[7] and his collaborators have now commenced a study of the influence of substituents in the phenyl nucleus of this compound. Introduction of the group ·Cl, ·Br, $\cdot NO_2$, ·Me, or ·OMe does not alter the selective action of the nitrosoarylhydroxylamine

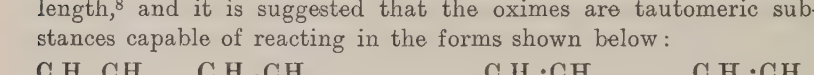
[4] *Ber.*, 1903, **36**, 57, 359; *A.*, 1903, i, 283, 286.
[5] *Ibid.*, 1916, **49**, 317; *A.*, i, 436.
[6] E. Bamberger and O. Baudisch, *Ber.*, 1909, **42**, 3577; *A.*, 1909, i, 977
[7] *Ibid.*, 1916, **49**, 172, 180, 191, 203; *A.*, i, 386, 387, 388, 389.

in forming internally complex salts, for, in these cases, only the salts with iron, copper, titanium, and zirconium are of internally complex nature. The circumstances are quite different when the substituent group is $\cdot O\cdot SO_2\cdot C_6H_4Me$, $\cdot OH$, $\cdot NH\cdot SO_2\cdot C_6H_4Me$, $\cdot NMe\cdot SO_2\cdot C_6H_4Me$, $\cdot NMe_2$, or $\cdot CHO$ in the ortho- or meta-position, for here the capability of forming internally complex salts is extended to nearly all the metals. To give an example, *o*-nitrosohydroxylaminophenyl 4-toluenesulphonate,

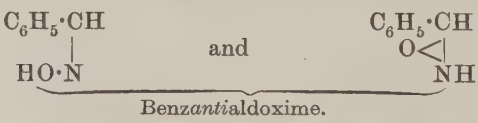
$$OH\cdot N(NO)\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me,$$

forms salts of this type with iron, copper, nickel, cobalt, chromium, manganese, vanadium, lead, cadmium, mercury, bismuth, aluminium, cerium, lanthanum, and thorium. Baudisch points out that the further developments of this work may have considerable importance for analytical and physiological chemistry.

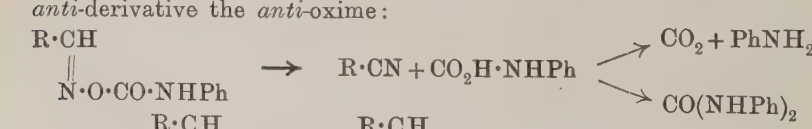
Oximes.—The isomerism of the oximes has been discussed at length,[8] and it is suggested that the oximes are tautomeric substances capable of reacting in the forms shown below:



Certain properties of the oximes are more readily explained by the assumption of an isomerism in this sense than by Beckmann's representation of a tautomerism as between the oxime and *iso*oxime formulæ:



In the course of this work it is shown that phenylcarbimide is not a suitable reagent for the determination of the configuration of the oximes, since it yields with *anti*-oximes a certain amount of the carbanilino-*syn*-derivative, and there is some evidence that this is, indeed, the primary product of the reaction. On hydrolysis, the carbanilino-*syn*-derivatives of the oximes behave similarly to the acyl derivatives, the *syn*-derivatives yielding a nitrile and the *anti*-derivative the *anti*-oxime:



The formation and degradation of the carbethoxy-derivatives takes place on similar lines.

[8] O. L. Brady and F. P. Dunn, *T.*, 1916, **109**, 650 *A.*, i 651.

Miscellaneous.—A new and interesting method of formation of azoimides is as follows: the aryldiazonium derivatives of trinitromethane readily decompose in the presence of moist ether into arylazoformhydroxamic acids, which yield the corresponding arylazoimide, carbon dioxide, and hydrogen when heated with aqueous alkali hydroxide[9]:

$$Ar\cdot N_2\cdot O\cdot ON{:}C(NO_2)_2 \longrightarrow$$
$$ArN{:}N\cdot CO\cdot NH\cdot OH \longrightarrow ArN_3 + CO_2 + H_2.$$

Phenylhydrazine is a useful reagent for effecting the reduction of azo- and bisazo-compounds to the corresponding amines, for the action proceeds rapidly in the cold or with gentle heating, and good yields of pure products may be obtained. Examples of its use are the reduction of benzeneazothymol to 6-aminothymol, bisazocarvacrol to diaminocarvacrol, $[OH:Me:Pr:(NH_2)_2 = 2:1:4:3:5]$, and benzeneazosalicylaldehyde to the phenylhydrazone of 5-amino-2-hydroxybenzaldehyde.[10]

Organometallic Compounds.

Antimony.—The interaction of triphenylstibine and antimony trichloride in xylene at 240° has been studied by many authors. J. Hasenbäumer[11] obtained phenylstibine dichloride in this way, and represented the reaction as follows:

$$Ph_3Sb + 2SbCl_3 = 3PhSbCl_2,$$

whilst A. Michaelis and A. Günther[12] obtained diphenylstibine chloride as the result of the reaction. G. T. Morgan and (Miss) F. M. G. Micklethwait[13] found that both substances were produced, and regarded the condensation as a balanced reaction in the sense indicated by the following equation:

$$(1a)\quad 2Ph_3Sb + SbCl_3 = 3Ph_2SbCl;$$
$$(1b)\quad Ph_2SbCl + SbCl_3 \rightleftharpoons 2PhSbCl_2.$$

G. Grüttner and M. Wiernik[14] have studied the reaction again, with important results. They have shown that phenylstibine dichloride is gradually converted into diphenylstibine chloride and antimony trichloride when distilled under diminished pressure,

$$2PhSbCl_2 \longrightarrow Ph_2SbCl + SbCl_3,$$

so that it is impossible to separate phenylstibine dichloride and diphenylstibine chloride quantitatively by fractional distillation. In order to investigate the composition of the product at different

[9] G. Ponzio, *Gazzetta,* 1915, **45**, ii, 12; 1916, **46**, ii, 56; *A.*, 1915, i, 1011 1916, i, 609.

[10] E. Puxeddu, *ibid.*, 1916, **46**, i, 62, 211; *A.*, i, 292, 435.

[11] *Ber.*, 1898, **31**, 2910; *A.*, 1899, i, 209

[12] *Ibid.*, 1911, **44**, 2316; *A.*, 1911, i, 1056.

T., 1911, **99**, 2286. [14] *Ber.*, 1915, **48**, 1749; *A.*, i, 96.

stages, it was necessary to devise a method for converting the constituents of the mixture into derivatives which would not undergo change. This was accomplished by treating the mixture with magnesium ethyl bromide, when antimony trichloride gave triethylstibine, phenylstibine dichloride phenyldiethylstibine, and diphenylstibine chloride diphenylethylstibine, whilst triphenylstibine remained unchanged. The alkylstibines were then separated by fractionation distillation, the amount of each was estimated, and from the results the composition of the original mixture was calculated. The authors conclude that the reaction takes place in two stages, the first proceeding most readily and quickly.

(2*a*) $Ph_3Sb + SbCl_3 = PhSbCl_2 + Ph_2SbCl$;
(2*b*) $Ph_2SbCl + SbCl_3 = 2PhSbCl_2$.

The fact that the use of a larger proportion of antimony chloride did not increase the yield of phenylstibine dichloride affords evidence against Morgan and Micklethwait's suggestion of an equilibrium (1*b*).

It may be noted that the reaction between triphenylbismuthine (2 mols.) and bismuth tribromide (1 mol.) in ether also gives rise to both diphenylbromobismuthine and phenyldibromobismuthine.[15]

Lead.—The study of mixed lead tetra-alkyls has been undertaken with the ultimate view of preparing asymmetric derivatives of lead.[16] It is found that lead tetramethyl and lead tetraethyl can be converted into lead trialkyl haloids by treatment with a solution of the halogen in carbon tetrachloride at $-75°$, and that lead trialkyl haloids react readily with magnesium alkyl haloids to yield mixed lead tetra-alkyls:

$$R_4Pb \longrightarrow R_3PbCl + R'MgCl \longrightarrow R_3R'Pb.$$

With one exception, all the lead trimethylalkyl and lead triethylalkyl compounds so prepared react with halogen under the above conditions and exchange one of the three methyl or ethyl groups present for halogen, thus yielding lead dimethyl-(or diethyl)-alkyl haloids, Me_2RPbCl; the exception is lead triethylmethyl, which yields lead triethyl haloids. It is hoped that the lead dimethyl-(or diethyl)-alkyl haloids will react with Grignard's reagents to give lead tetra-alkyls, $Me_2RR'Pb$, containing three different alkyl groups. A mixed lead tetra-aryl, namely, lead diphenyldi-*o*-tolyl, $PbPh_2(C_6H_4Me)_2$, has been obtained by the action of lead diphenyldi-iodide on magnesium *o*-tolyl bromide.[17]

[15] F. Challenger, *T.*, 1916, **109**, 250; *A.*, i, 347.
[16] G. Grüttner and E. Krause, *Ber.*, 1916, **49**, 1125; *A.*, i, 684.
[17] K. Lederer, *ibid.*, 349; *A.*, i, 446.

Sodium.—The preparation of disodio-derivatives of compounds containing a C:C, C:N, or N:N linking, for examples, of stilbene, benzylideneaniline and azomethane, is recorded in the patent literature.[18] On treatment with water, the alkali metal is replaced by hydrogen, whilst carbon dioxide converts the compounds into the corresponding carboxylic acids.

Tellurium.—A number of diaryl ditellurides and diaryl tellurides have been prepared by the action of magnesium aryl haloids on tellurium dihaloids, and their properties, which resemble those of the selenium analogues, have been studied.[19]

FRANK LEE PYMAN.

PART III.—HETEROCYCLIC DIVISION.

THE continuance of the war has again made the compilation of the Report a matter of some difficulty, owing to the inaccessibility of certain enemy journals; and the same cause has resulted in the inclusion under the current year of some few papers which were not available on account of their publication abroad in the later months of last year. It seemed better to include these in the 1916 Report rather than to pass them over in silence, although technically they belong to an earlier volume.

During the year, the decline in certain branches of the subject has been marked. The study of plant colouring matters has apparently ceased. The chemistry of the blood and the bile, which used to bulk largely in the Reports, has become practically stagnant. Chlorophyll seems to excite no interest at present; and even the supposed synthesis of the substance mentioned in last year's Report has produced only one theoretical paper disagreeing with the authors' conclusions.[1]

The chemistry of the alkaloids, once so fruitful a field, has been comparatively neglected in the last twelve months, although the synthesis of histidine by Pyman and the investigation of cryptopine and protopine by Perkin stand out from a mass of otherwise somewhat confused material. In this connexion, the Reporter may perhaps be permitted to hope that papers like these will be preferred as models in place of the mass of ill-digested data and hasty conclusions which seem to form the stock-in-trade of certain

[18] W. Schlenk, D.R.-P., 292310; *A.*, i, 683.

[19] K. Lederer, *Ber.*, 1915, **48**, 1345, 1422, 1944, 2049; 1916, **49**, 334, 345, 1071, 1076, 1082; *A.*, 1915, i, 1056; 1916, i, 40, 141, 208, 392, 646, 647.

[1] T. Jona, *Mon. Sci.*, 1916, [v], **6**, i, 149; *A.*, i, 660.

foreign workers. Fully half the trouble entailed in reading papers on the alkaloids is attributable to the fact that investigators hasten to publish a few isolated results as soon as these are obtained, instead of holding back the material until it falls into its proper perspective among other data.

Last year it was necessary to chronicle the discovery of new heterocyclic groupings in which fresh elements appeared as members of the rings. This year the field has been much enlarged by the introduction of silicon, arsenic, and titanium among the elements capable of producing heterocyclic compounds. On the other hand, the announcement of the discovery of silver pentazole, which was mentioned in last year's Report, has turned out to be unfounded.

The pyrrole group still retains its place as a centre of interest; but it will be noted that the trend of investigation has passed away from the naturally occurring pyrrole compounds and is tending toward the purely synthetic types.

The flavone and diflavone group has again been the object of research, and much interesting material may yet be expected in this branch of the subject.

Taken as a whole, the heterocyclic series still retains the attention of many workers; but the results of their investigations are more diffused than in past years, so that an air of scrappiness is inseparable from any wide survey of the subject. Consciousness of this defect was present in the mind of the Reporter in drawing up the following pages, and it is to be feared that readers will feel as he himself did. If this should unfortunately be the case, he trusts that they will mingle sympathy with condemnation, for the task of compiling the Report has been no light one.

Some New Heterocyclic Types.

Up to a very recent date, the heterocyclic compounds, although differing widely among themselves in character and complexity of structure, bore a certain family resemblance to one another owing to the fact that the non-carbon atoms of the ring were drawn entirely from among three elements: oxygen, sulphur, and nitrogen. There might be various non-carbon atoms in the same ring; but, generally speaking, the chemistry of the heterocyclic series consisted in ringing the changes on these three elements. Two years ago, the discovery of rings in which mercury atoms were included threw a fresh light on the possibilities which were still open, and last year silicon, selenium, arsenic, and titanium were

added to the list of elements capable of playing their part as members of cyclic chains.[2]

The current year has expanded this group. Penta-, hexa-, and hepta-atomic ring systems have been prepared containing, in addition to the usual carbon members, one of the elements phosphorus, antimony, bismuth, tin, lead, and thallium, whilst further syntheses of heterocyclic arsenic and silicon compounds have been devised.[3]

The general method of synthesis may be illustrated by a concrete example. In the preparation of phenyl*cyclo*pentamethylenephosphine

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>PPh,$$

$\alpha\epsilon$-dibromopentane is chosen as the starting point, and is first converted into the corresponding organo-magnesium derivative. The latter is allowed to react with the compound, $PPhCl_2$, in ethereal solution. After evaporation of the solvent, the required substance is obtained by distillation under diminished pressure. When a five-membered chain is desired, $\alpha\delta$-dibromo- or dichloropropane is substituted for the pentane derivative, whilst if a different element be needed as a ring member, it is inserted by using the appropriate substance of the type $RXHal_2$, in which X is the element to be introduced and R is any organic univalent radicle.

In this way, six-membered cyclic derivatives of phosphorus, arsenic, antimony, and bismuth have been produced, which yield the usual "onium" compounds with ethyl iodide and with mercuric salts. *p*-Tolyl*cyclo*pentamethylenephosphine, $C_5H_{10}P\cdot C_6H_4Me$, is distinguished by giving an additive compound with carbon tetrachloride, while ethyl*cyclo*pentamethylenebismuthine, $C_5H_{10}BiEt$, is so readily oxidised that, if it is poured on paper, it inflames spontaneously in the air.

Turning to the behaviour of the corresponding five-membered rings, it is found that they can be synthesised even more readily than the six-membered compounds. The phosphorus and arsenic atoms in these five-membered cyclic chains appear to be endowed with specially active residual affinity, for the substances form additive compounds with many solvents, inorganic haloids, etc.

The simple cyclic nature of the new substances is shown by the fact that their molecular weights are normal and also by their behaviour on fission with chlorine, the parent chloro-paraffin being

[2] See *Ann. Reports*, 1914, 126; 1915, 129.

[3] G. Grüttner and M. Wiernik, *Ber.*, 1915, **48**, 1473; *A.*, 1916, i, 92; G. Grüttner and E. Krause, *Ber.*, 1916, **49**, 437; *A.*, i, 443.

regenerated. The boiling points of the compounds agree with von Braun's rule, the replacement of two ethyl groups by the pentamethylene ring having the effect of raising the boiling point by approximately 50°.

Similar results have been obtained by another worker in the case of arsenic compounds.[4] It is proposed that the nomenclature of the new series should be brought into line with that of the pyridine group by terming the arsenic analogue of pyridine *arsedine*, while the substance corresponding with piperidine would receive the name *arsepedine*. For example, methyl*cyclo*pentamethylenearsine would be called 1-methylarsepedine. It must be admitted that if much work is done in this field in the future, it will be necessary to find some convenient short substitute for the present somewhat cumbrous nomenclature.

The So-called Pentazole Compounds.

In last year's Report[5] a description was given of a series of substances which were assumed to contain a cyclic chain of five nitrogen atoms. The class of compounds seemed of such interest that it is with regret that the writer feels constrained to insert an extra adjective in the title of this section. It appears, however, that the observations of Lifschitz are erroneous, for the results of Curtius and his colleagues[6] point to a conclusion different from that arrived at by the earlier worker.

Lifschitz, by treating cyanotetrazole with hydrazine hydrate, obtained a substance which he termed pentazolylacetohydrazidine, and to which he ascribed the structure

$$\begin{matrix} \mathrm{N{:}N} \\ | \\ \mathrm{N{:}N} \end{matrix}\!\!>\!\mathrm{N{\cdot}CH_2{\cdot}C(:NH){\cdot}NH{\cdot}NH_2}.$$

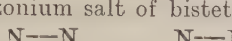
Curtius and his collaborators observe, however, that when cyanogen is passed into aqueous azoimide for the preparation of cyanotetrazole, the latter substance is not the only product, for a varying amount of a further condensation product is produced, namely, bistetrazole:

$$\mathrm{N_3H + C_2N_2 \longrightarrow CHN_4{\cdot}CN};$$
$$\mathrm{CHN_4{\cdot}CN + NH_3 \longrightarrow C_2N_8H_2}.$$

When the reaction mixture is treated with hydrazine hydrate in

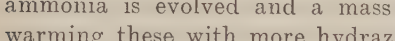
[4] E. V. Zappi, *Bull. Soc. chim.*, 1916, [iv], **19**, 151, 290; *A.*, i, 575, 683.
[5] P. 142.
[6] T. Curtius, A. Darapsky, and E. Müller, *Ber.*, 1915, **48**, 1614; *A.*, 1916, i, 84.

absolute alcohol at 0°, a white product separates out, which appears to be the bishydrazonium salt of bistetrazole,



This formula seems to be established by the fact that the compound yields benzaldazine when shaken with benzaldehyde.

When the filtrate from this substance is boiled under reflux, ammonia is evolved and a mass of yellow crystals formed. On warming these with more hydrazine hydrate to complete the reaction, there remains, after the ammonia has all been evolved, an orange-yellow mass which corresponds with Lifschitz's pentazole derivative. The substance, however, appears to be actually ditetrazyldihydrotetrazine,



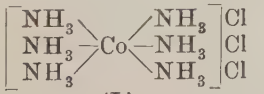
and an account is given of reactions corresponding with this structure.

Although the compounds in question are extremely complicated, it seems beyond doubt that Curtius is right, and that Lifschitz did not succeed in producing a pentazole derivative, so that the search for a five-membered ring containing only nitrogen atoms remains open to those who wish to investigate that field.

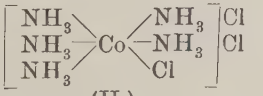
Heterocyclic Theories of the Complex Salts.

It will be recalled that the earliest attempts to explain the nature of the cobaltammines were based on structural ideas. The work of Blomstrand, continued by Jörgensen, laid the foundations of our knowledge in this region of the subject, and progress along these lines produced results of considerable interest. Later, Werner advanced his so-called "co-ordination theory," which, in its turn, stimulated investigation and led to the amassing of a vast amount of data by its author and his collaborators. For a time, the "co-ordination theory" held the field; but there have been signs in recent years that a return to the older structural ideas is beginning, although the newer views differ very considerably from the original Blomstrand-Jörgensen proposals.

The weaknesses of the "co-ordination theory" have recently been criticised by Friend.[7] Taking as his examples the two compounds formulated by Werner as follows,



(I.)



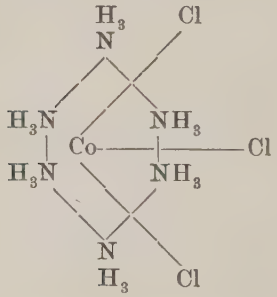
(II.)

[7] J. A. N. Friend, *T.*, 1916, **109**, 715; *A.*, i, 637.

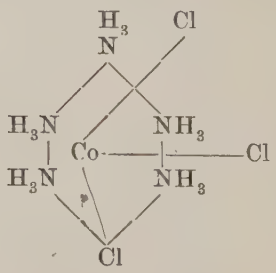
Friend points out that the three dissociable chlorine atoms are supposed to hover vaguely about the nucleus. Such an hypothesis has certain advantages, owing to its indefiniteness, "because it may be interpreted to accord with almost any theory or suggested grade of chemical combination," but, on the other hand, it has its weaknesses. For example, the "co-ordination theory," "whilst assuming a definite valency for cobalt, nitrogen, and hydrogen atoms, denies an equally definite valency to chlorine unless, as in the case of the pentammine salt (II), it happens to fall within the nucleus." Friend also directs attention to the fact that the "co-ordination theory" ascribes to cobalt a valency of six, which is opposed to ordinary experience. The idea of "principal" and "auxiliary" valencies does not get over the difficulty, since it now seems to be admitted that there is no real difference between them. Thirdly, Friend points out that in the "co-ordination theory" the chlorine atoms directly attached to a metallic atom are supposed to lose their ionising power—a postulate which is in direct contradiction to ordinary chemical ideas.

In view of these difficulties, Friend advocates a return to structural conceptions of the metalammines, and his own views seem to require much less straining of chemical conventions than is necessitated by the "co-ordination theory."

Taking the two substances mentioned above, Friend assumes that they each contain a nuclear six-membered ring, in the centre of which, but not attached to it, lies the cobalt atom, held there by physical forces only. The chlorine atoms directly attached to the cobalt atom possess their normal power of changing into ions, while the chlorine atom which forms part of the ring is not capable of ionisation. In this scheme, all the atoms retain the valencies known to be associated with them according to ordinary chemical ideas, so that there is no need for hypotheses as to "main" or "auxiliary" valencies.



(I.)

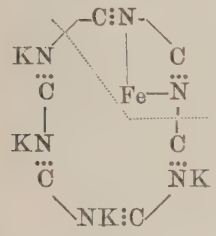


(II.)

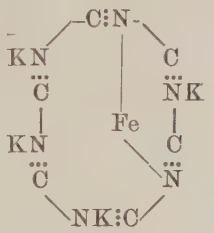
A test case between the two theories is supplied by the behaviour

of potassium ferrocyanide. Briggs[7a] has shown that this salt occurs in two modifications, which he termed the α- and β-forms. Now since, on the "co-ordination theory," the potassium atoms are hovering uncertainly around the ferrocyanide nucleus, no isomerism can be ascribed to their positions relative to one another; and since the nucleus is symmetrical, on the "co-ordination theory," the arrangement of its constituents can afford no explanation of the isomerism. (Werner himself admits that isomerism of the ferro- and ferri-cyanides cannot be covered by his views.)

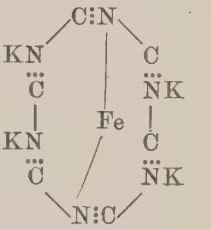
On the other hand, Friend's theory furnishes an explanation, not only of the existence of two ferrocyanides, but also of the occurrence of potassium ferricyanide in isomeric forms. There are three possible structures for potassium ferrocyanide:



Ortho-form.

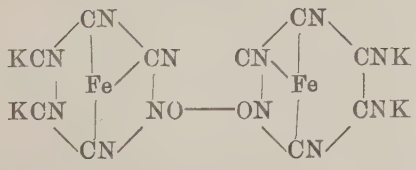


Meta-form.



Para-form.

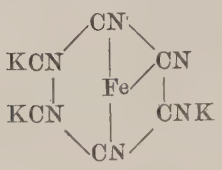
Of these, the ortho-form is simply the double salt, $4KCN,Fe(CN)_2$, as is indicated by the dotted line through the formula. The meta- and para-forms represent the two isomeric ferrocyanides. Briggs has shown that the α-ferrocyanide is stable in alkaline solution, but passes into the β-form in neutral or acid solvents. Now when an acid solution of potassium ferrocyanide (β-form stable) is treated with nitric oxide it yields nitroprussic acid, which exists in one form only. An examination of the formulæ of the meta- and para-structures will show that this can only occur if the β-salt has a symmetrical structure—which proves it to be the para-form. On this basis, the structure of potassium nitroprusside is as shown below:



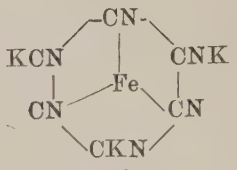
Similar reasoning applies to the case of the isomeric ferricyanides. Since the β-ferricyanide is stable in acid solution, it is

[7a] Briggs, *T.*, 1911, **99**, 1019.

derivable from the β-ferrocyanide, and hence the two salts are represented thus:

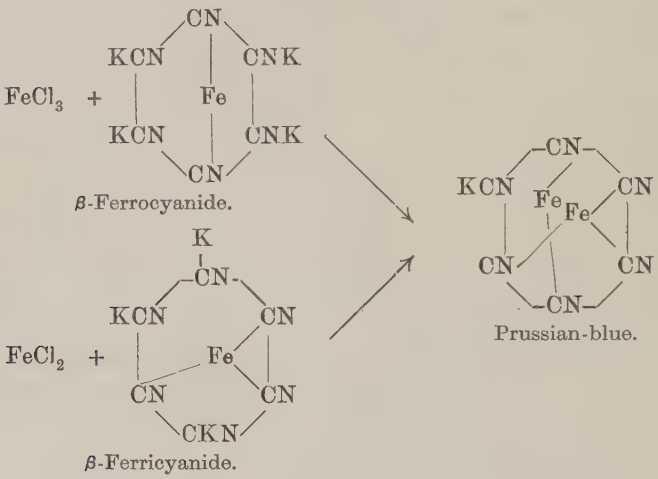


β-salt.



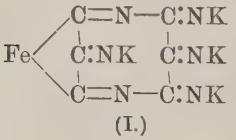
α-salt.

The identity of the Prussian-blues obtained from ferric salts and a ferrocyanide or from ferrous salts and a ferricyanide, is a matter which fails of satisfactory explanation on the "co-ordination theory"; but on Friend's theory it is easily explicable. The formulæ below will make the matter clear:

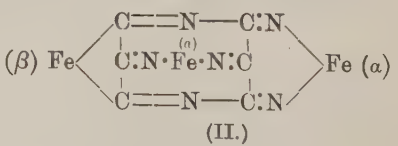


The existence of the three known soluble Prussian-blues can also be accounted for by Friend's theory.

Another attempt to explain the nature of the ferro- and ferricyanides has been made by Denigès.[8] On his scheme, potassium ferrocyanide is represented by (I) and ferrous ferrocyanide by (II), whilst the production of Williamson's salt from potassium ferrocyanide at a red heat is shown in the equation below (III):

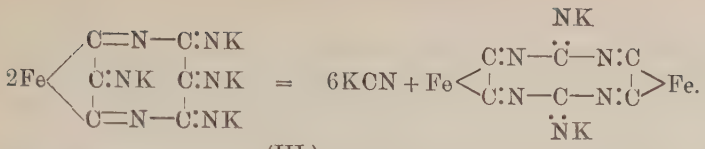


(I.)



(II.)

[8] G. Denigès, *Bull. Soc. chim.*, 1916, [iv], **19**, 79; *A.*, i, 310.



(III.)

Other examples of the applicability of the author's views are given in the original paper. They differ to some extent from the results arrived at by Friend, since in most of his formulæ Denigès regards iron as bivalent, whereas Friend employs tervalent iron atoms also.

These papers indicate a welcome revival of structural ideas in the region of the complex salts. The conceptions of structure which have been so laboriously and skilfully built up in one branch of chemistry are probably equally applicable in fresh fields, although their growth may be slower than it was among the purely carbon compounds, and it is encouraging to note the success of the newer views in just those particular cases which the old "co-ordination theory" failed to explain.

Friend's theory has been criticised by Turner,[9] but the criticism fails on certain points. Turner considers that the retention of the cobalt atom by the "shell" is "not convincing," and he finds fault with Friend's views on the ground that in their present form they give no reason to assume optical activity in the case of certain metalammines. He objects also to chlorine being treated as a tervalent element, and he quotes Friend as referring "to tervalent chlorine as the usual form in which combined chlorine is to be found." What Friend actually says in the passage referred to by Turner is that "the chlorine atom in the ring (on the Friend theory) is tervalent and saturated," there being no reference to the tervalency of the element being "usual." This rather detracts from the accuracy of the criticism. The possible tervalency of chlorine can scarcely be a matter of dispute.

Another line of argument employed by Turner concerns the stability of bridged linking in a six-membered ring; but as many bridged rings are known among the alkaloids and terpenes the point scarcely seems a strong one, even if it be granted that analogy can be stretched so far as to include the peculiar type of ring assumed by Friend.

A further criticism is based by Turner on an examination of the "positive" and "negative" valencies exerted by nitrogen atoms; but this argument has considerably lost its point, since the discovery of triphenylmethyltetramethylammonium,[10] in which all the

[9] E. E. Turner, *T.*, 1916, **109**, 1130.

[10] W. Schlenk and J. Holtz, *Ber.*, 1916 **49**, 603; *A.*, i, 385.

valencies of the nitrogen atom are saturated by hydrocarbon radicles.

Turner states that it has been shown (although not yet published) that sodium α- and β-ferrocyanides are identical, and not isomeric. If this be so, the extension of Friend's theory to cover this case will be unnecessary. The accounts of the experimental work in the matter will be awaited with interest, as the subject is important; in the meantime, judgment must be reserved until the evidence is made known.

Steric Hindrance and Reactivity.

Although questions of steric hindrance do not now excite the interest shown in them twenty years ago, when the subject was novel, yet scarcely a year passes without the addition to our knowledge of some new facts in this region of chemistry. At the same time, our outlook on the problem has changed. Instead of the purely mechanical hypothesis, which depended upon the assumption of actual collisions of atoms or interference in space with their free passage to and fro, we are now apt to look for some deeper causes in the case of inhibitions which in earlier years would have been definitely ascribed to steric hindrance pure and simple.

A very good example has come to light during the past year.[11] It has been shown that tertiary aromatic amines can be condensed with formaldehyde to form para-substituted benzyl alcohols, and a study has been made of the effect produced by substituents in the phenyl nucleus. At the same time, the influence of the same substituents on the capacity of the tertiary amino-group to yield quaternary ammonium salts has been examined. The figures below give the relative yields in the two cases under comparable conditions.

Derivative of dimethylaniline	*o*-Methyl	*o*-Chloro-	*o*-Bromo-	*o*-Methoxy-
Yield of benzyl alcohol, per cent.	6	36	45	60
Yield of ammonium salt, per cent.	7·6	15·6	16	100

An examination shows that the two reactions can scarcely be influenced by steric hindrance to exactly the same extent. In the one case, the reaction takes place at the nitrogen atom, in the ortho-position with respect to the substituent, while in the second reaction the active sphere is at the other end of the benzene nucleus, greatly removed from the substituent so far as mere spatial conditions are concerned. Yet, as the figures show, both reactions are affected in the same manner by the presence of the substituent

[11] J. von Braun, *Ber.*, 1916, **49**, 1101; *A.*, i, 647.

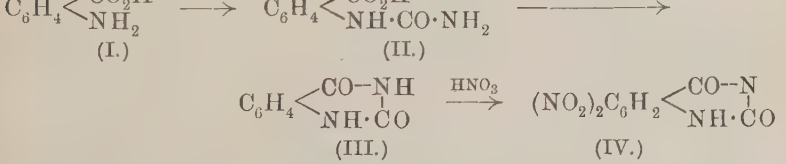
atoms. The only conclusion which can be drawn is that the hindrance in this case has its origin, not in purely spatial sources, but rather in some arrangement of residual affinity within the molecule. The colour of the alcohols—they are yellow oils—tends to confirm this view, for if both the alcoholic radicle and the amino-group retained their usual structure, there is no apparent reason for any development of visual colour in such compounds.

Similar peculiarities mark the results in some other cases. In testing the reactions of formaldehyde and methyl iodide with kairoline (1-methyltetrahydroquinoline), the reactive hydrogen atom in the last compound was found to be much more readily displaced than might have been anticipated, whilst the reactivity of the nitrogen atom also was enhanced, in spite of the fact that it has adjacent to it the second ring of the quinoline nucleus. Steric influences alone would have exactly the opposite effect.

Somewhat similar conditions appear to come into play in the case of 2:3-dimethyl-γ-benzthiopyran, which forms additive compounds with a large number of metallic salts.[12] Although the evidence is somewhat scanty, it seems probable that intramolecular rearrangement accompanies the formation of these additive compounds.

A New Indicator.

Hitherto there has been no satisfactory indicator for hydrogen-ion concentrations lying between the limits of 6 and 8 on the Sörensen scale, but this year the synthesis of dinitrobenzoylene-carbamide has filled the gap.[13] The substance has the structure shown below (IV); the first nitro-group lies in the position 6, but the orientation of the second one has not yet been established.



(I.) (II.) (III.) (IV.)

The steps in the preparation of the new indicator are shown in the above formulæ. Anthranilic acid (I) is treated with potassium cyanate solution, yielding a precipitate of *o*-carbamidobenzoic acid (II). By adding sodium hydroxide and cooling, the sodium salt of the acid separates out, and when this is dissolved in boiling water and acetic acid is added, benzoylenecarbamide (III) is

[12] H. Simonis and A. Elias, *Ber.*, 1916, **49**, 1116; *A*, i, 660.

[13] M. T. Bogert and G. Scatchard, *J. Amer. Chem. Soc.*, 1916, **38**, 1606; *A.*, i, 672.

obtained in a 92 per cent. yield. After nitration, this substance gives the required indicator (IV).

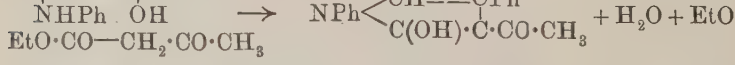
The indicator is colourless at the limit 6 and is greenish-yellow at the limit 8. It is very slightly affected by neutral salts, can be used at 100° or in the cold, and is not more affected by proteins than is *p*-nitrophenol. With ammonia and hydrochloric acid it gives sharp end-points, but it cannot be used for the titration of carbonates.

The Pyrrole Group.

Researches in this branch of the heterocyclic series continue with almost unabated vigour, and in view of the importance of the pyrrole derivatives from the physiological side, any extension of our knowledge in this field must be welcomed. In previous years, the members of the pyrrole group round which most controversy centred were those connected with the problem of the bile constituents, but during the past twelve months the main subjects of investigation have been substances of a much simpler character.

To commence with the synthetic section of the subject, mention must be made of a modification of a method already known. It will be recalled that the interaction of amino-ketones and β-ketonic esters gives rise to pyrrole derivatives, and it has now been shown [14] that compounds containing a secondary amino-group can be used in place of the amino-ketones without inhibiting the capacity for reaction.

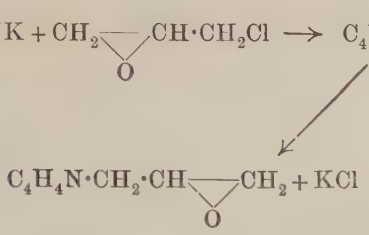
When phenacylaniline is boiled with either ethyl or methyl acetoacetate, the product of the reaction appears to be 5-hydroxy-4-acetyl-1 : 3-diphenylpyrrole, which seems to be formed by a condensation expressible as follows:



Pyrrole derivatives containing a substituted propyl group as a side-chain might become of interest if they could be applied to a synthesis of alkaloids, such as tropine or hygrine, so that a recently devised method [15] of preparing such members of the pyrrole series may at a later date have an important bearing on the synthesis of naturally occurring substances. The method consists in allowing the potassium derivative of pyrrole to react with epichlorohydrin, and the reaction appears to take place in two stages. In the first stage, the potassio-pyrrole attaches itself to the oxide

[14] G. K. Almström, *Annalen*, 1916, **411**, 350; *A.*, i, 568.
[15] K. Hess and H. Fink, *Ber.*, 1915, **48**, 1986; *A.*, 1916, i, 158.

ring, whilst the second stage entails the elimination of potassium chloride:



The reaction also gives rise to a dimeride of the new ring compound.

The reaction between potassio-pyrrole and dichloro*iso*propyl acetate (acetyldichlorohydrin) is not quite so simple as this. From the fact that the product contains a new diacetylpyrrole, it seems probable that the hydrin decomposes into epichlorohydrin and acetyl chloride. The properties and reactions of the pyrryl propylene oxide have been studied, and certain bicyclic pyrrole derivatives have thus been obtained.

One of the products of the oxidation of pyrrole is a substance known as pyrrole-black; but along with this there are formed, according to the conditions of the experiment, other substances having colours ranging from brown to yellowish-white.[16] Several of these compounds have been examined, and it appears that their compositions are very similar to that of pyrrole-black itself. The yellowish-white substance appears to have a marked tendency to furnish blue compounds. A study of the action of hydrogen peroxide in acetic acid solution has resulted in some results of interest, but the details cannot be given here.

A new oxidation reaction[17] has been worked out which applies to the cases of some pyrrolidine and piperidine derivatives. By means of formaldehyde, secondary hydrindamines of the pyrrolidine group can be converted into tertiary amino-ketones:

$$C_4H_8N\cdot CH_2\cdot CHMe\cdot OH \longrightarrow C_4H_7NMe\cdot CH_2\cdot COMe.$$

When other aldehydes are used, the reaction gives rise to 1-alkylpyrrolidyl ketones; and when primary alcohol derivatives are employed in place of secondary alcohols, the resulting products are aldehydes.

The reaction is rendered more interesting owing to the marked influence exerted on it by the solvent employed. In alkaline solu-

[16] A. Angeli and L. Alessandri, *Atti R. Accad. Lincei*, 1916, [v], **25**, i, 761; *A.*, i, 667.

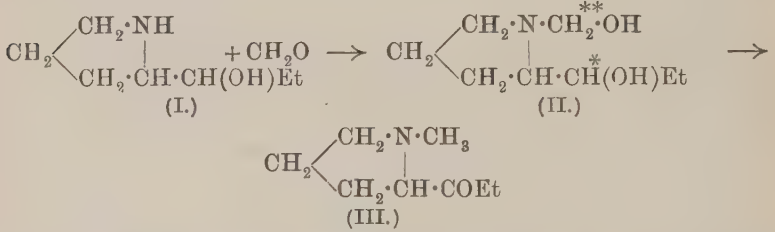
[17] K. Hess, F. Merck, and C. Uibrig, *Ber.*, 1915, **48**, 1886; *A.* 1916, i, 67.

tions the results are quite different from those obtained when an acid solvent is used:

$$C_4H_8N\cdot CH_2\cdot CH_2\cdot OH + CH_2O \xrightarrow{\text{alkaline}} C_4H_7NMe\cdot CH_2\cdot CH_2\cdot OH$$

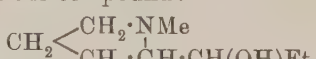
$$C_4H_8N\cdot CH_2\cdot CH_2\cdot OH + CH_2O \xrightarrow{\text{acid}} C_4H_7NMe\cdot CH_2\cdot CHO$$

The exact processes which take place during the reaction are not yet quite clear; but it seems likely that there is an intermediate product of the aldehyde-ammonia type produced, so that the stages in the case of pyrrolidyl*iso*propyl alcohol might be formulated as follows:

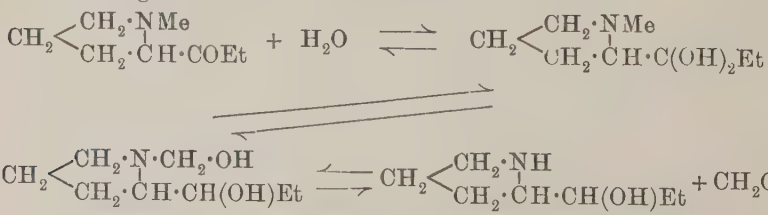


The aldehyde–ammonia compound is formed as shown in (II), and then the group marked ** oxidises the group marked * so as to produce the substance (III).

If a third reagent is present which is more readily oxidisable than the group marked with the single asterisk, this new reagent is oxidised instead and the alcoholic radicle is shielded. Thus in presence of formic acid the reaction results in the formation of carbon dioxide and the compound:



A curious reversal of the oxidation reaction is produced in some cases by the action of hydroxylamine on the end-product. Hydroxylamine appears to favour the addition of water to the ketones, and at the end of the reaction formaldehyde may be detected in the solution. The reverse reaction is supposed to take the following course:



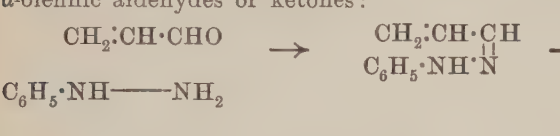
An application of the reaction in a wider field would be of

interest. In the case of piperidine [18] the action of formaldehyde solution leads to the formation of almost equal quantities of methylpiperidine and methylenepiperidine.

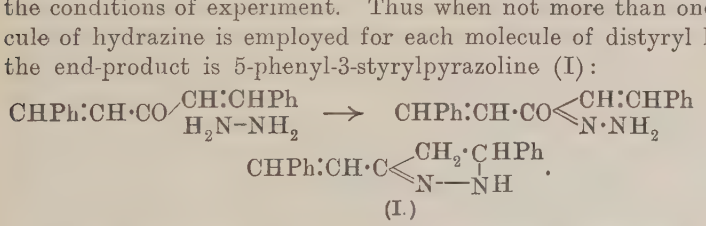
The Conversion of Pyrazoline Derivatives into cyclo*Paraffins.*

It will be recalled that when pyrazolinecarboxylic acids are heated they decompose with the evolution of nitrogen and the formation of acids derived from the *cyclo*paraffins. An attempt [19] has been made to extend the application of this reaction into a fresh field; and the results, although not quite so simple as had been expected, are none the less of value, and are, perhaps, even more interesting than they would have been had they fallen out exactly as anticipated.

Pyrazolines are obtained when hydrazine is allowed to react with α-olefinic aldehydes or ketones:

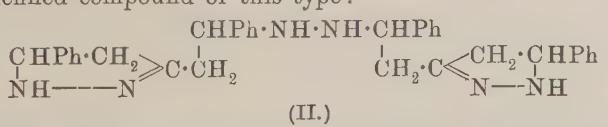


and it was assumed that distyryl ketone would react in a manner similar to that which is observed in the case of simpler substances. It appears, however, that the reaction is very much influenced by the conditions of experiment. Thus when not more than one molecule of hydrazine is employed for each molecule of distyryl ketone, the end-product is 5-phenyl-3-styrylpyrazoline (I):



(I.)

If, on the other hand, hydrazine is employed in excess, the reaction takes place as before, but in addition two molecules of the newly formed pyrazoline combine with one molecule of hydrazine, giving a well-defined compound of this type:



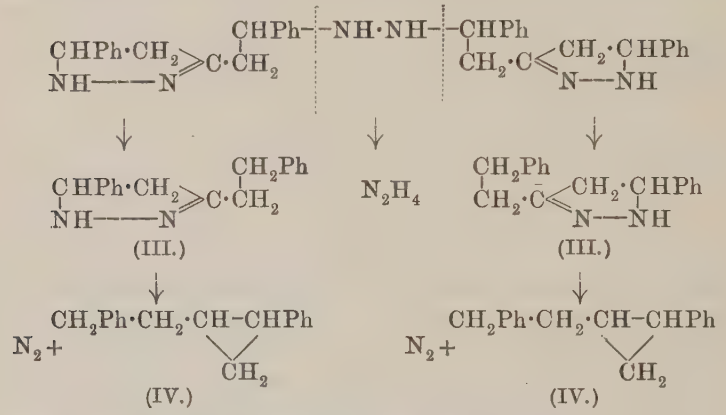
(II.)

The reaction obviously parallels that which takes place between hydroxylamine and distyryl ketoxime, addition of the amino-compound taking place at the remaining double linking of the ketone.

[18] K. Hess and F. Wissing, *Ber.*, 1915, **48**, 1907; *A.*, 1916, i, 74.

[19] N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1819; *A.*, 1916, i, 290.

These two pyrazoline derivatives behave differently when heated. The compound (I) when heated alone gives rise to 3:4-diphenyl-*cyclo*pentene, $\begin{matrix}CHPh{-}CH\\ |\\ CHPh{\cdot}CH_2\end{matrix}\!\!>\!CH$. The compound (II), on the other hand, suffers various types of decomposition according to the conditions chosen. When heated alone, it breaks down in either of two ways: (1) it yields, in the first place, hydrazine and 5-phenyl-3-styrylpyrazoline (compound I), which then gives the *cyclo*paraffin derivative already mentioned; or (2) it undergoes scission at the hydrazine residue, giving rise to 5-phenyl-3-β-phenylethylpyrazoline (III), which, on further heating with potassium hydroxide, produces 1-phenyl-2-β-phenylethyl*cyclo*propane (IV):



When heated with hydrochloric acid the compound (II) gives the hydrochlorides of hydrazine and of the compound (I). This hydrochloride of the compound (I), when further heated, suffers a loss of hydrogen chloride, and this decomposition is accompanied by intramolecular change, which gives rise to the hydrochloride of a dipyrazoline base, as shown below:

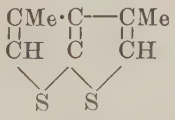
It will be seen from the above that even a comparatively simple reaction is capable of ramifying in many interesting directions.

Some Sulphur Compounds.

In former years the reporter found it possible to arrange a rough classification of the researches which had been carried out in this branch of the heterocyclic series; but during the past twelvemonth the investigations of this group have been so isolated and varied in their objects that it is almost impossible to separate the papers into definite categories. Thus the present section must necessarily appear somewhat scrappy in its form; the only division line which could be drawn was between compounds containing sulphur atoms alone in addition to carbon ones as ring-members and other compounds which contain further elements in the ring in addition to sulphur ones.

The simplest compounds requiring mention are the new sulphones of the thiophen series, which have been obtained from the parent substances by the action of 30 per cent. hydrogen peroxide in glacial acetic acid solution.[20] When tetraphenylthiophen is treated in this way it yields tetraphenylthiophen dioxide, $C_4Ph_4SO_2$. This substance appears to be a true sulphone, and differs in character from the compound which results from the action of hydrogen peroxide on thiophen itself. From the theoretical point of view, the new sulphones are not without interest, as they mark a case in which the sulphur atom of thiophen is forced out of its usual inactivity, and their formation points to the likelihood that the inertness of the thiophen sulphur atom with respect to alkyl iodides is not ascribable to steric influences, but must be sought in some chemical phenomenon.

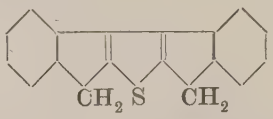
A rather unexpected result[21] has been observed when *n*-octane is heated with sulphur in a sealed tube for some hours at 270—280°. A thiophen, $C_8H_{12}S$, and a thiophthen, C_8H_8S, are formed, although in small yield. It is suggested that the first stage in the reaction is the conversion of the normal carbon chain into a branch-chain of the following type, $CHMe_2{\cdot}CHMe{\cdot}CHMe_2$, which is attacked by the sulphur, with the formation of a compound having the following structure:



The action of sulphur on indene, hydrindene, and *cyclo*pentadiene has led to curious results.[22] A vigorous reaction ensues

[20] O. Hinsberg, *Ber.*, 1915, **48**, 1611; *A.*, 1916, i, 66.
[21] W. Friedmann, *Ber.*, 1916, **49**, 1344; *A.*, i, 735.
[22] *Ibid.*, 50; *A.*, i, 415.

when indene and sulphur are heated together, and a compound, which appears to be a di-indenethiophen of the following formula, is produced, along with a second substance having a composition corresponding with $C_{36}H_{24}S$:



The action of sulphur on hydrindene gave a substance, $C_{18}H_{12}S$, which was formed in an almost pure condition, whilst with di*cyclo*pentadiene a simpler substance is produced, which has the composition $C_{10}H_{12}S$.

An interesting series of sulphur derivatives has been obtained by the action of phosphorus pentasulphide on *o*-benzoicsulphinide.[23] The first product of the reaction appears to be thio-*o*-benzoicsulphinide, which is then converted to some extent into 2:3-dithiosulphindene:

$$C_6H_4\langle\begin{matrix}CS\\-S-\end{matrix}\rangle S.$$

Better yields of this last compound are produced by acting on "thiosaccharin" with phosphorus pentasulphide:

$$C_6H_4\langle\begin{matrix}CO\\SO_2\end{matrix}\rangle NH \longrightarrow C_6H_6\langle\begin{matrix}CS\\SO_2\end{matrix}\rangle NH \longrightarrow C_6H_4\langle\begin{matrix}CS\\-S-\end{matrix}\rangle S,$$

2:3-Dithiosulphindene, when heated with dilute alkali carbonate or hydroxide solution, is degraded to an open-chain substance, as shown in the following scheme:

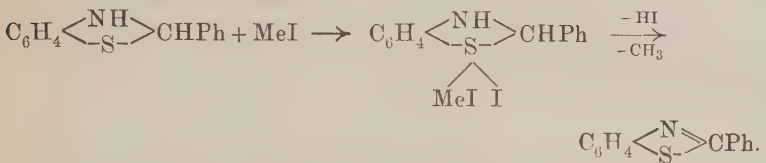
$$C_6H_4\langle\begin{matrix}CS\\-S-\end{matrix}\rangle S \longrightarrow SH\cdot C_6H_4\cdot CO_2H \longrightarrow CO_2H\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot CO_2H.$$

A new synthesis[24] of 1-thiochromones (benzthiopyrones) and 1:4-dithiochromones (4-thiobenzthiopyrones) has been worked out as follows. Thiolbenzenes with free ortho-positions are condensed with β-ketonic esters in the presence of phosphoric oxide, and in this way thiochromones are formed in the same manner as the oxygen analogues. When these thiochromones are melted with phosphorus pentasulphide, 1:4-dithiochromones are produced. Thus from thiophenol and methyl acetoacetate, 2:3-dimethylbenzthiopyrone is produced, which, on treatment with phosphorus pentasulphide, gives 4-thio-2:3-dimethylbenzthiopyrone,

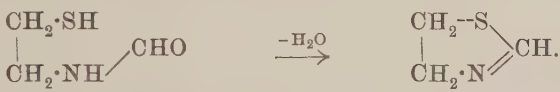
$$C_6H_4\langle\begin{matrix}CO\cdot CMe\\S--CMe\end{matrix}\rangle \xrightarrow{P_2S_5} C_6H_4\langle\begin{matrix}CS\cdot CMe\\S--CMe\end{matrix}\rangle.$$

[23] A. Mannessier, *Gazzetta*, 1916, **46**, i, 231; *A.*, i, 231.
[24] H. Simonis and A. Elias, *Ber.*, 1916, **49**, 768; *A.*, i, 499.

Heterocyclic compounds containing nitrogen and sulphur atoms in their rings have been studied in some detail during the year. A very simple synthesis of benzthiazolines[25] has been found to take place when *o*-aminothiophenolhydrochlorides are shaken in aqueous-alcoholic solution with aldehydes. The reduction of the thiazoline to the corresponding thiazole has been noted when the thiazoline is heated with methyl iodide. Apparently the reaction follows the course shown in the scheme below:



Other thiazole derivatives have been synthesised[26] by removing the elements of water from the formyl derivatives of aminoethyl or aminopropyl thiols:



A new class of indigoid dyes has been prepared.[27] Hitherto, compounds of this type have been confined to those in which both the groups at the ends of the ring are cyclic in character, but this year a successful attempt has been made to synthesise aliphatic–aromatic indigoid dyes. The older dyes were prepared by the action of compounds containing the group $\cdot CO \cdot CH_2 \cdot$ on the anilides of diketones, but when it was desired to apply this reaction to open-chain ketones, such as methyl ethyl ketone, it was found that the ketomethylene group alone did not possess sufficient reactivity to permit the reaction to take place. Accordingly, a β-diketone was substituted for the monoketone, with the result that condensation was found to occur quite readily. In this manner, dyes were formed which contained the chromophoric group $\cdot CO \cdot C\therefore C \cdot CO \cdot$. Curiously enough, however, the new dyes have no affinity for vegetable or animal fibres.

Some work on hydroxy- and methoxy-derivatives of "thioindigo" may also be mentioned here, although for details the reader is referred to the original paper.[28] The results prove that compounds of this class behave as normal dyes.

Space forbids the summarisation of papers on the naphtha-

[25] M. Claasz, *Ber.*, 1916, **49**, 1141; *A.*, i, 669.
[26] S. Gabriel, *ibid.*, 1110; *A.*, i, 668.
[27] W. Herzog and A. Jolles, *ibid.*, 1915, **48**, 1574; *A.*, 1916, i, 74.
[28] P. Friedlaender, *ibid.*, 1916, **49**, 955; *A.*, i, 674.

sultams[29] and the derivatives of sulphazone.[30] These must be consulted in the original. As to the oxidation of thiodiphenylamine by means of mercuric oxide or mercuric acetate,[31] it will be sufficient to mention that the product is a heterocyclic compound of the following structure:

$$S<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>N\cdot N<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S.$$

The conversion of phenazonium perbromide into the bromide of methylene-blue takes the following course:

$$C_6H_4\ll\begin{matrix}N--\\SBr\end{matrix}>C_6H_4+4Br+2NHMe_2\ =$$

$$Me_2N\cdot C_6H_3\ll\begin{matrix}N--\\SBr\end{matrix}>C_6H_3\cdot NMe_2+4HBr.$$

The reaction is stated to be very suitable for a lecture experiment.[32]

The Coumarin Group.

One or two points of interest have come to light in this field during the year. When coumarin is warmed with 20 per cent. sodium hydrogen sulphite the solution deposits sodium hydrocoumarinsulphonate,[33] which crystallises with one molecule of water:

$$C_6H_4<\begin{matrix}O\text{—}CO\\CH_2\cdot CH\cdot SO_3Na\end{matrix}.$$

Although solutions of the sodium salt are neutral, they can be titrated with sodium hydroxide. This peculiar behaviour seems to find its explanation in a series of reactions. The first action of the sodium hydroxide is to eliminate the sulphonic group with the formation of coumarin and sodium sulphite, whilst this is followed by a combination of sulphite and coumarin to produce a sulphonic derivative of hydrocoumaric acid:

$$C_6H_4<\begin{matrix}-O-CO\\CH_2\cdot CH\cdot SO_3Na\end{matrix}\xrightarrow{NaOH}C_6H_4<\begin{matrix}O---CO\\CH:CH\end{matrix}+Na_2SO_3+H_2O.$$

$$C_6H_4<\begin{matrix}-O-CO\\CH:CH\end{matrix}+Na_2SO_3\longrightarrow C_6H_4<\begin{matrix}OH\ \ CO_2Na\\CH_2\cdot CH\cdot SO_3Na\end{matrix}.$$

If the solution is evaporated with excess of alkali present, a coumarate is formed, and this reaction provides a rapid method of converting coumarin into coumaric acid. On the other hand, if

[29] T. Zincke and C. Jülicher, *Annalen*, 1916, **411**, 195; *A.*, i, 426.
[30] M. Claasz, *Ber.*, 1916, **49**, 350; *A.*, i, 424.
[31] L. Pesci, *Gazzetta*, 1916, **46**, i, 103; *A.*, i, 289.
[32] F. Kehrmann and R. Speitel, *Ber.*, 1916, **49**, 53; *A.*, i, 435.
[33] F. D. Dodge, *J. Amer. Chem. Soc.*, 1916, **38**, 446; *A.*, i, 413.

the dry residue left on evaporating the solution is heated with acetic anhydride, the hydrocoumarinsulphonate is regenerated, and from it coumarin can be obtained by adding 20 per cent. sodium carbonate. Thus the following series of reversible changes can be carried out:

Coumarin $\rightleftharpoons$ hydrocoumarinsulphonate $\rightleftharpoons$
hydrocoumaric-sulphonate $\rightleftharpoons$ coumaric acid.

A study of the hydrolysis of coumarin leads to the following results: In alcoholic solution with a large excess of alkali, coumarin is completely hydrolysed. If then the alkali is partly neutralised, coumarin begins to be formed, even although the solution is still markedly alkaline. By the formation of the coumarin, the solution tends to become more alkaline again, and the process can be repeated by the further neutralisation of the alkali up to the point when coumarin and its salts come into equilibrium.

Some modifications in the experimental details of coumarin syntheses are reported, which are said to yield better results than those given by the ordinary method.[34]

A synthesis of thiocoumarin by distilling *o*-thiolcinnamic acid with phosphoric oxide appears to produce good yields.[35]

A peculiar example of autoxidation has been observed in the coumarin series.[36] A specimen of 1:4-dimethylcoumaran-2-one, which had been stored for some months in a corked bottle, was found to have become converted almost entirely into 4-acetoxy-*m*-toluic acid. It is supposed that this change is due to the addition of oxygen to the ethylenic linking of the enolic form of the coumaranone:

$$C_6H_3Me\begin{cases}C(OH)\\ \quad O\end{cases}\!\!>CMe + O_2 = C_6H_3Me\begin{cases}\text{---}C(OH)\cdot O\\ O\cdot CMe\text{---}O\end{cases} =$$

$$C_6H_3Me\begin{cases}CO_2H\\ OAc\end{cases}.$$

As might be expected, the reaction was much more rapid when the compound was freely exposed to air.

Bromination appears to lead to analogous results. Thus when a chloroform solution of dimethylcoumaranone is treated with its own weight of bromine at 0°, bromo-*p*-cresotic acid,

$$HO\cdot C_6H_2MeBr\cdot CO_2H,$$

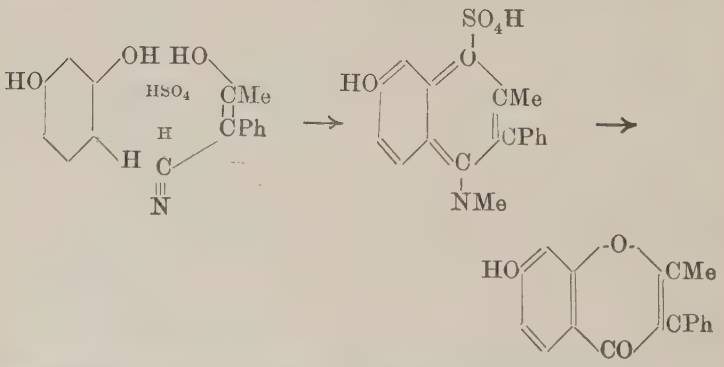
separates out.

[34] H. Simonis and Goldenzweig, *Ber.*, 1915, **48**, 1583; *A.*, 1916, i, 57.
[35] H. Simonis and A. Elias, *ibid.*, 1916, **49**, 763; *A.*, i, 498.
[36] K. von Auwers, *ibid.*, 820; *A.*, i, 496.

Benzopyrones and Flavone Derivatives.

In last year's Report[37] reference was made to the blue iodine adsorption compounds formed by certain pyrone derivatives, and this year has added a certain amount to our knowledge in that field. It is found[38] that 8-phenyl-γ-benzopyrone-2-carboxylic acid dissolved in alkali and poured into *N*/100-potassium tri-iodide solution containing excess of acid gives an intense blue coloration, whilst an alcoholic solution of the ester shows a similar behaviour. Even more sensitive in character is 8-phenyl-γ-benzopyrone itself, since it yields a blue adsorption compound with iodine up to a dilution of *N*/4000. A 1 per cent. alcoholic solution of γ-phenanthropyrone gave blue tints with aqueous iodine solutions up to *N*/2000. It appears from the results obtained up to the present that the presence of benzene nuclei in the pyrone molecules has a marked effect on the formation of the blue compounds.

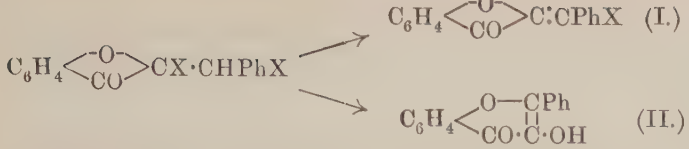
A modification of the flavone synthesis has been devised,[39] in which nitriles (instead of esters) of acetoacetic acids are condensed with phenols. The imines thus formed can be hydrolysed to flavones. Thus when acetylphenylacetonitrile is condensed with resorcinol and sulphuric acid, the reaction takes the following course:



The phenols which react best are those which contain methyl or hydroxyl substituents.

A study of the effect of substituents on reactions has been carried out in the flavonol synthesis from benzylidenecoumaranones.[40] Halogen-additive compounds of benzylidenecoumaranones are decomposed by alkalis in either of two ways, as indicated below:

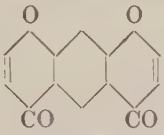
[37] *Ann. Reports*, 1915, 144.
[38] A. R. Watson, *T.*, 1916, **109**, 303; *A.*, i, 414.
[39] B. N. Ghosh, *ibid.*, 105; *A.*, i, 281.
[40] K. von Auwers, *Ber.*, 1916, **49**, 809; *A.*, i, 496.



The relative amounts of the two end-products formed is governed by the nature of the substituents introduced into the molecule. Thus ortho- or para-substituents in the benzene ring with respect to the oxygen atom of the coumaranone ring considerably weaken the reaction (II), so that the chief products of the reaction in these circumstances are flavonols, whilst meta-substituents have the opposite effect. Substituents in the phenyl ring of the benzylidene nucleus also affect the decomposition. In fact, the presence in that ring of a nitro-group or two methoxy-radicles is sufficient to inhibit the formation of any flavonol.

The Diflavone Group.

In last year's Report [41] attention was directed to the synthesis of compounds derived from the hitherto unknown nucleus, diflavone:



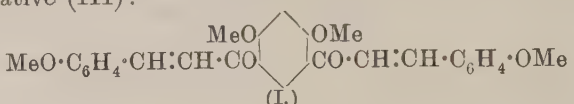
Although these substances are highly coloured, they are not capable of acting as mordant dyes, owing to the absence of auxochromic groups, and this year attempts have been made to prepare other derivatives of the series which contain such radicles, and which will therefore be comparable with the dyes of the mono-flavone compounds. In the course of this investigation,[42] certain points of interest have arisen which serve to illustrate the marked influence exerted on the progress of reactions by the conditions under which they are carried out.

The condensation of 4:6-diacetyl-1:3-dihydroxybenzene with anisaldehyde was tried in four different ways. In the first place, the reaction was carried out in boiling alcoholic solution in the presence of sodium hydroxide, and in this case the end-product was 4:6-di-*p*-methoxycinnamoyl-1:3-dihydroxybenzene (I). Secondly, an aqueous solution of the diacetyl derivative, anisaldehyde, and sodium hydroxide was allowed to remain at the ordinary tempera-

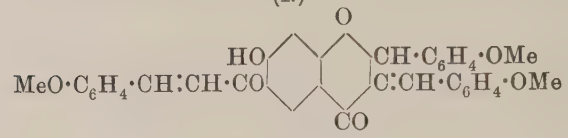
[41] *Ann. Report*, 1915, 154.

[42] H. Ryan and J. Algar, *Proc. Roy. Irish Acad.*, 1916, **32** [*B*], 185; *A.*, i, 662; H. Ryan and M. J. Walsh, *Proc. Roy. Irish Acad.*, 1916, **32** [*B*], 193; *A.*, i, 663.

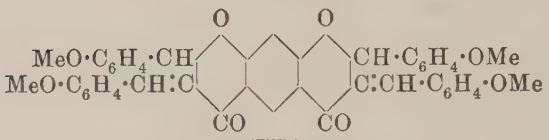
ture for six months, whereby a stereoisomeride of the previous end-product was produced. Thirdly, the diacetyl derivative and anisaldehyde were condensed in hot alcoholic solution in presence of hydrogen chloride, and in this way a diflavanone derivative (II) was obtained after some heating. Finally, if the same operation is conducted at the ordinary temperature, the product is the diflavanone derivative (III):



(I.)

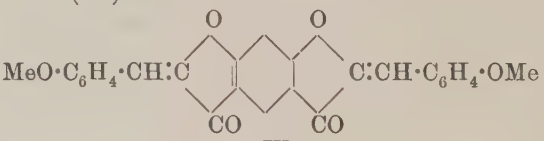


(II.)



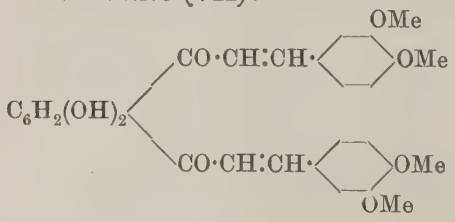
(III.)

When either of the compounds (I) is treated with sodium acetate and acetic anhydride it yields a diacetate. The two diacetates on treatment with bromine in chloroform solution give tetrabromides, and these react with alcoholic potassium hydroxide with the formation of the same crystalline derivative, which appears to be a dicoumaranone (IV):

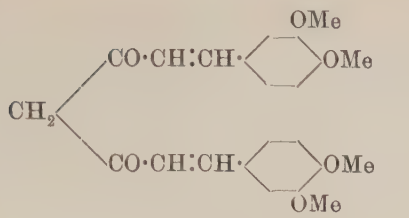


(IV.)

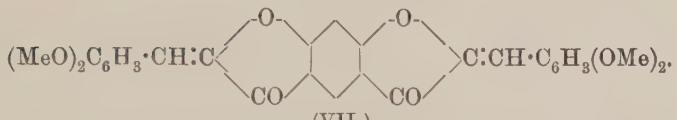
When veratraldehyde was substituted for anisaldehyde, and the first of the methods mentioned above was chosen, the result was a substance (V) which, on subsequent acetylation and treatment with bromine and alcoholic potassium hydroxide, yielded a dicoumaranone derivative (VII):



(V.)



(VI.)



(VII.)

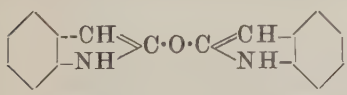
The similarity between the new compound (V) and the curcumin dimethyl ether, the structure of which is shown in (VI), is obvious at a glance, and an examination was made of the comparative tinctorial properties of the two substances. The dicoumaranone has no effect on unmordanted wool, whilst with tin and aluminium mordants it gave pale canary and pale lemon colours, curcumin under the same condition yielding orange-red and orange-yellow tints. It is thus clear that the new substance has tinctorial effects which are slight in comparison with those of curcumin.

Further research in this group will be awaited with interest, as it is clear that the compounds are very sensitive to changes in the reaction conditions, and much valuable information as to the effect of slight alterations in reagents may be expected.

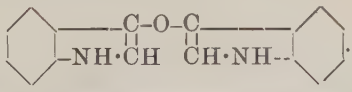
The Indole Group.

A new indole synthesis [43] has been discovered, based on the elimination of carbon dioxide and water from *o*-aldehydophenylglycine under the action of acetic anhydride and sodium acetate, whilst a series of photochemical syntheses of indole derivatives [44] has been worked out.

Autoxidation of indoles in the presence of sunlight [45] has yielded some interesting substances, one of which appears to be an ethereal derivative of indole having the following structure:



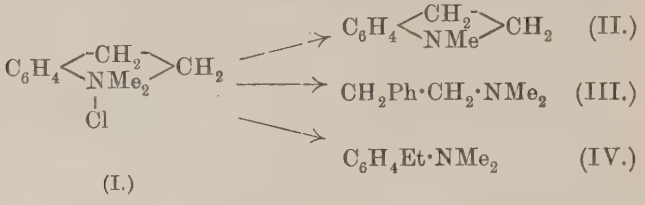
or



A study of the reduction of certain indole derivatives by means of sodium amalgam has shown that various end-products are

[43] W. Gluud, D.R.-P., 278282; *A.*, i, 288.
[44] P. Pfeiffer, *Annalen*, 1916, **411**, 72; *A.*, i, 327.
[45] B. Oddo, *Gazzetta*, 1916, **46**, i, 323; *A.*, i, 502.

formed according to the conditions of the experiment.[46] Thus, 1:1-dimethyldihydroindolium chloride (I) is converted by the reducing agent into three other bases, of which (II) is formed to the extent of 75 per cent. of the total yield, (III) to the extent of 8 per cent., whilst (IV) makes up the remaining 17 per cent.

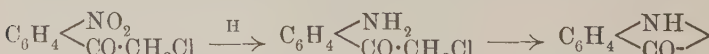


Indigotin and its Derivatives.

A rapid method of atmospheric oxidation of indigotin and similar substances has been devised,[47] which depends on exposing them to air in solutions of compounds of high boiling point, such as quinoline or phenanthrene. Thus, in boiling phenanthrene solution, 1 gram of indigotin can be completely oxidised in half an hour. It seems possible that this method might be applied to other cases of oxidation.

Another new method of oxidation[48] depends on the utilisation of triethylphosphine as an oxygen carrier. The phosphine is converted into an unstable phosphine peroxide, $PEt_3{:}O_2$, which then parts with some of its oxygen to the indigotin, and is itself reduced to the corresponding oxide. The reaction can be utilised as a lecture experiment.

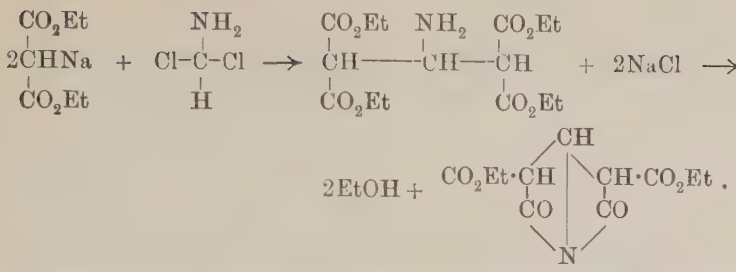
Substituted indigotins can be produced[49] by the reduction of substituted chloronitroacetophenones by boiling with zinc and 30 per cent. acetic acid. The reaction follows the course shown below:



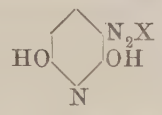
The Pyridine Group.

Some syntheses of pyridine derivatives have been worked out during the last year. Thus, the condensation of ethyl sodiomalonate with the sesquihydrochloride of hydrocyanic acid gives a 50 per cent. yield of ethyl 2:6-diketodinicotinate,[50] in accordance with the following scheme:

[46] J. von Braun and L. Neumann, *Ber.*, 1916, **49**, 1283; *A.*, i, 742.
[47] P. Friedlaender and N. Roschdestwensky, *ibid.*, 1915, **48**, 1841; *A.*, i, 80.
[48] N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2129; *A.*, i, 290.
[49] F. Bodinus, *Chem. Zeit.*, 1916, **40**, 326; *A.*, i, 429.
[50] L. Gattermann and A. Skita, *Ber.*, 1916, **49**, 494; *A.*, i, 419.



The ester is readily convertible into dihydroxypyridine, from which a number of derivatives have been produced, of which the most interesting are azo-dyes corresponding with the formula



Pyridine bases are also obtainable by the condensation of ketones with amides.[51] Thus, when acetone (2 mols.) and acetamide (1 mol.) are heated together in a sealed tube to 250°, 2:4:6-trimethylpyridine is formed. 2:4:6-Triphenylpyridine is formed similarly from benzamide and acetophenone. In neither case, however, is the yield a good one. From analogy, it might be expected that pyridine itself could be produced by this reaction from acetaldehyde and formaldehyde, but experiments in this direction have been unsuccessful. α-Picoline is formed in small yield from paracetaldehyde and acetamide. Various pyridine derivatives[52] have been isolated by hydrolysing casein in presence of methylal, the latter compound being utilised as a permanent source of formaldehyde. In this reaction, primary, secondary, and tertiary bases are produced, but quinoline derivatives do not seem to be formed.

Reference was made in last year's Report[53] to the action of sodium on pyridine. Since then, further work has been done in this field.[54] The first product of the interaction between sodium and pyridine is the substance, $(C_5H_5N)_2Na$, and it has been shown that, on heating at 130°, this is converted into the simpler substance, C_5H_5NNa, by loss of 1 molecule of pyridine. Analogous results are obtained when sodium is replaced by lithium or potassium, two compounds of each metal being formed. It seems possible that a further investigation of this problem may throw interesting light on some questions of valency.

A somewhat peculiar behaviour has been observed in the addi-

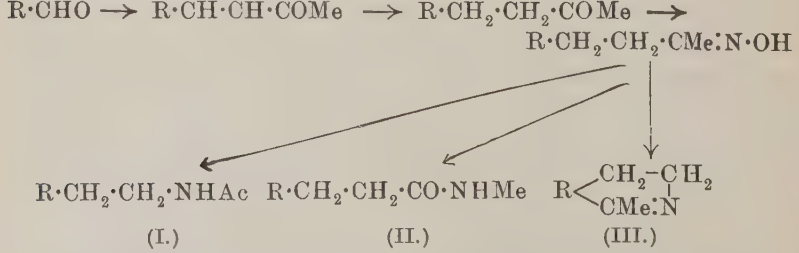
[51] A. Pictet and P. Stehelin, *Compt. rend.*, 1916, **162**, 876; *A.*, i, 571.
[52] A. Pictet and T. Q. Chou, *ibid.*, 127; *A.*, i, 226.
[53] *Ann. Report*, 1915, 141.
[54] B. Emmert, *Ber.*, 1916, **49**, 1060; *A.*, i, 454.

tion of amyl nitrite to pyridine.[55] When the two substances are mixed in a sealed tube, no interaction appears to occur even after some weeks, but if the tube is opened, crystals appear in a day, which prove to be pyridine nitrate. When amyl nitrate and pyridine are allowed to remain together, no reaction takes place. It is possible that the reaction can be explained by the decomposition of the alkyl nitrite in the presence of moisture, and that the nitrous acid thus set free attaches itself to the pyridine and then undergoes oxidation, but it is also possible that the pyridine decomposes the nitrite, with the formation of amylene and nitrous acid.

A peculiar catalytic action of thionyl chloride has been observed in some applications of the Friedel-Crafts' reaction to the pyridine series.[56] When absolutely pure materials are employed, no reaction takes place between pyridine or quinoline derivatives and acetyl or benzoyl chloride in the presence of aluminium chloride. A similar inhibition is noted when aromatic hydrocarbons and pyridinecarboxylic acid chlorides are employed. In neither case is any ketone produced. If, however, a trace of thionyl chloride is added to the mixture, the reaction proceeds readily along the normal lines, and ketones are produced in good yields. The merest trace of thionyl chloride seems sufficient to start the reaction. If the acid chlorides have been prepared by the action of thionyl chloride on the acids, it is found that after exhaustion at the ordinary temperature enough thionyl chloride remains behind to start the process of ketone synthesis.

The Quinoline Group.

A new and simpler synthesis of *iso*quinolines has been devised.[57] Aromatic aldehydes are condensed with acetone; the products are reduced to saturated ketones; *syn*-oximes of these are prepared; and finally the Beckmann rearrangement is brought into play. Three products are thus obtained; (I) the acetyl derivative of the amine; (II) the methylamide of the acid; and (III) a 1-methyl-3 : 4-dihydro*iso*quinoline.



(I.) (II.) (III.)

[55] C. W. Addy and A. K. Macbeth, *T.*, 1916, **109**, 754; *A.*, i, 668.
[56] R. Wolffenstein and F. Hartwich, *Ber.*, 1915, **48**, 2043; *A.*, i, 222.
[57] A. Kaufmann and R. Radosevič, *ibid.*, 1916, **49**, 675; *A.*, i, 502.

By proper selection of the experimental conditions, it is possible to procure a good yield of (III).

Some oxidation[58] and reduction[59] reactions of quinoline derivatives have been studied, but it is unnecessary to give details here.

Mercuric Acetate as a Reagent in Alkaloidal Chemistry.

The use of mercuric acetate as a mild oxidising agent has long been known, but recently[60] it has been shown that this substance can be utilised, not only qualitatively, but quantitatively, since it is possible to recover and weigh the sparingly soluble mercurous acetate which results from the reaction. Not only so, but owing to the mildness of the reagent's action, it is sometimes possible to conduct the reaction in stages, which are quite clearly defined. Thus, for example, when *N*-methylbulbocapnine is oxidised by means of alcoholic iodine, it loses two hydrogen atoms, whilst a third is replaced by iodine. When mercuric acetate is employed, the result is a simple removal of two hydrogen atoms from the compound if the reaction is carried out at the ordinary temperature, but on the water-bath a further stage of oxidation takes place and an extra molecule of mercuric acetate is used up. In a similar manner, corydaline is converted first into a dihydrocorydaline and then into a tetrahydro-derivative. Other examples given are the oxidations of *d*-canadine, *r*-laudanosine, and papaverine. It seems that the reagent will prove of great value in further investigations.

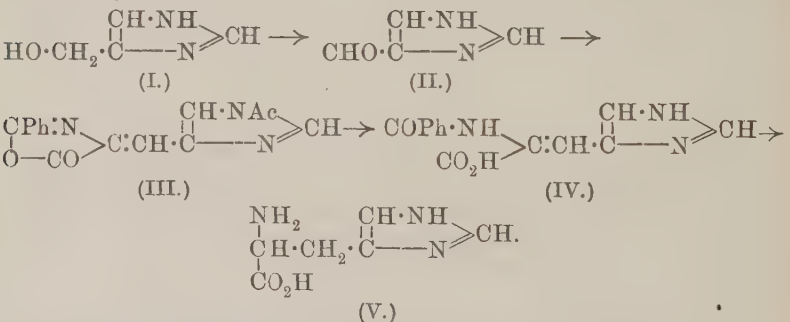
Some New Alkaloid Syntheses.

The constitution of damascenine (from *Nigella damascena*) was established by Ewins[61] in 1912, and this year a new method of synthesis[62] has been discovered which enables the alkaloid to be procured in quantity. The starting material is commercial 8-hydroxyquinoline, which, by the action of methyl sulphate and potassium hydroxide, is converted into 8-methoxyquinoline. Further treatment with methyl sulphate produces an additive compound having the structure

[58] R. Boehm and K. Bournot, *Ber.*, 1915, **48**, 1570; *A.*, 1916, i, 75.
[59] J. von Braun and E. Aust, *ibid.*, 1916, **49**, 501; *A.*, i, 421.
[60] J. Gadamer, *Arch. Pharm.*, 1915, **253**, 274; *A.*, 1916, i, 736.
[61] Ewins, *T.*, 1912, **101**, 544.
[62] A. Kaufmann, E. Rothlen, and B. Vargolici, *Ber.*, 1916, **49**, 578; *A.*, i, 417.

Oxidation of this last substance, by means of aqueous potassium permanganate in the presence of magnesium sulphate, gives rise to a mixture of methoxy-*N*-methylisatin and formyldamasceninic acid, $MeO\cdot C_6H_3(NMe\cdot CHO)\cdot CO_2H$. The latter compound, on treatment with 5 per cent. methyl-alcoholic hydrogen chloride, is converted into damascenine itself (methyl 2-methylamino-3-methoxybenzoate). If formyldamasceninic acid is treated with dilute hydrochloric acid, it is hydrolysed to formic acid and damasceninic acid, whilst the action of concentrated hydrochloric acid leads to the formation of the hydrochloride of damasceninic acid.

A new synthesis of histidine has been accomplished in the following manner.[63] The 4-hydroxymethyl derivative of glyoxaline (I) is prepared in the usual way, and is oxidised with chromic acid, yielding glyoxalineformaldehyde (II). The latter compound is then condensed with hippuric acid by means of acetic anhydride, and the result is 2-phenyl-4-[1-acetylglyoxaline-4-methylidene]-oxazolone (III). When this oxazolone is boiled with very dilute aqueous sodium carbonate, the acetyl group is removed and the oxazolone ring opens, and if the calculated quantity of an acid is then added, the result is the formation of α-benzoylamino-β-glyoxaline-4-acrylic acid (IV), which can be reduced to benzoyl-*r*-histidine by the usual methods. Histidine (V) is finally obtained by hydrolysis.



The yields obtained in the various reactions are satisfactory.

The Morphine Group.

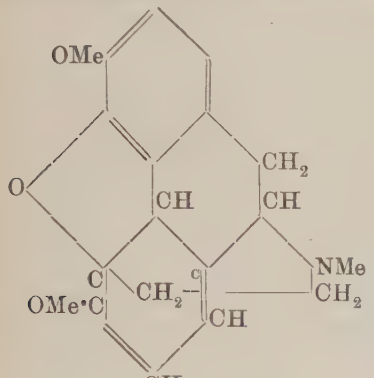
A considerable amount of investigation during the year has centred on the study of morphine alkaloids in which the *N*-methyl group is replaced by cyanogen or hydrogen.[64] The preparation of such compounds has been made easier by utilising the action of a chloroform solution of cyanogen chloride or bromide on a similar

[63] F. L. Pyman, *T.*, 1916, **109**, 186; *A.*, i, 335.

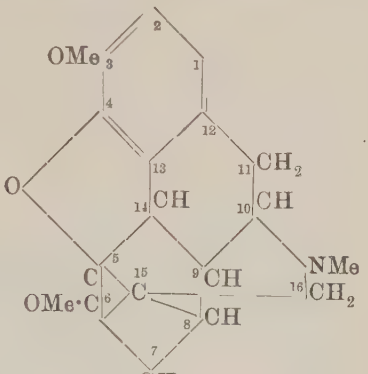
[64] J. von Braun, *Ber.*, 1916, **49**, 750; *A.*, i, 500; *ibid.*, 977; *A.*, i, 665.

solution of the acetylated alkaloid.[65] From the cyano-derivatives, ether may be obtained by the action of sodium ethoxide and an alkyl iodide. The physiological action of many of these morphine derivatives has been studied.[64]

The reduction of thebaine and phenyldihydrothebaine[66] has been carried out in various ways with the object of determining whether or not thebaine contains ethylenic linkings in its structure, as Knorr suggested in his formula (I). The results are regarded as disproving the presence of double bonds in the molecule, and the formula (II) has been suggested as more in accordance with the evidence.

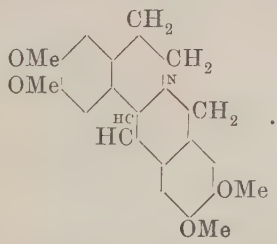


(I.)



(II.)

By the action of methylal on tetrahydropapaverine,[67] a single base is produced (in contradistinction from the action of acetal, which gives rise to two coralydines). The new compound is a lower homologue of the coralydines, and has been named nor-coralydine. It has the structure shown in the formula below.



Papaverine has the property of condensing with aldehydes (or substances capable of giving rise to aldehydes), and this power seems to be shared by many of the papaverine derivatives.[68]

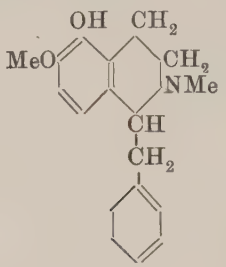
[65] F. Hoffmann, La Roche & Co., D.R.-P., 289273 ; *A.*, i, 417.

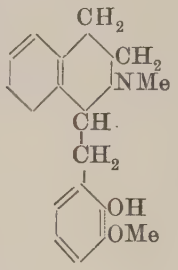
[66] M. Freund and E. Speyer, *Ber.*, 1916, **49**, 1287 ; *A.*, i, 738.

[67] A. Pictet and T. Q. Chou, *ibid.*, 370 ; *A.*, i, 418.

[68] Société pour l'Industrie Chimique à Bâle, Fr. Pat., 475654 ; *A.*, i, 221.

Further work has been done on berberine derivatives. Azo-derivatives of the dihydroberberine series have been prepared,[69] the azo-group replacing the reactive hydrogen atom in the position 4. The demethylation of *iso*berberine[70] has been accomplished, and it is now assumed that this substance has one or other of the following structures:



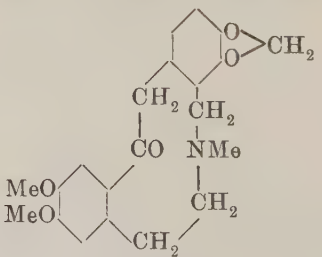


Cryptopine and Protopine.

An important paper[71] has been published on these substances and their derivatives. Fortunately, it appeared in the Transactions, and is thus easy of access, for it is clearly impossible to summarise even the salient points in the space at the Reporter's disposal. All that can be done is to set down some of the more important matters with which it is concerned, and leave the reader to examine the data and arguments in the original.

Cryptopine is an alkaloid occurring in opium and having the composition $C_{21}H_{23}O_5N$. It is optically inactive and has a marked physiological action.

Perkin, from a study of the various decompositions of the alkaloid, draws the conclusion that its behaviour is best represented by the formula



Cryptopine.

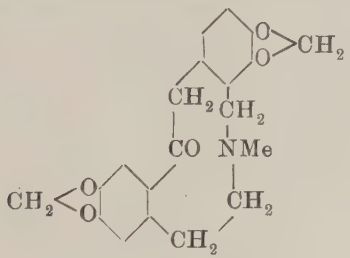
He points out, however, that this formula does not account for the

[69] M. Freund and K. Fleischer, *Annalen*, 1916, **411**, i; *A.*, i, 325.
[70] M. Scholtz, *Arch. Pharm.*, 1915, **253**, 622; *A.*, 1916, i, 416.
[71] W. H. Perkin, jun., *T.*, 1916, **109**, 815.

fact that cryptopine yields neither oxime nor semicarbazone, although the structure given above contains the group $\cdot CO \cdot CH_2 \cdot$, nor does the alkaloid react with *iso*amyl nitrite and sodium ethoxide, as might be expected from a structure such as this. Further, the ten-membered ring is a somewhat unusual grouping, although, since the synthesis of nonamethylene, there seems to be no reason for rejecting a formula on that ground alone. The structures of the methylcryptopines are also considered.

Various reactions of cryptopine have been studied—nitration, oxidation with different reagents, and also sundry decompositions of the alkaloid. A very full account of the salts of cryptopine is given.

Protopine, $C_{20}H_{19}O_5N$, is a very widely distributed alkaloid which occurs along with cryptopine in opium. The two alkaloids differ in composition by one carbon and four hydrogen atoms, and since they both give many similar reactions, it seems probable that they are closely akin to one another. Cryptopine (see above) contains two methoxy-groups which are not found in protopine, and it appears probable that these two groups are replaced, in the latter alkaloid, by a single methylenedioxy-radicle. Perkin has brought a large amount of evidence to show that the structure of protopine may reasonably be regarded as this:



Protopine.

It is impossible to go further into detail, as the evidence is complex and does not lend itself to summarisation, but the reader is advised to consult the original, which extends to more than two hundred pages.

Yohimbine.

The nature of this interesting substance has given rise to a considerable amount of controversy. In last year's Report[72] it was assumed that the identity of yohimbine and quebrachine had been established, as seemed to be demonstrated by the work of Fourneau

[72] *Ann. Report*, 1915, 163.

and Page.[73] Spiegel,[74] however, refuses to accept this evidence. It appears that Fourneau and Page compared yohimbine with a specimen of "quebrachine" furnished by Merck, but Spiegel maintains that this preparation is really a mixture of yohimbine and mesoyohimbine.

As to the constitution of yohimbine, Barger and Field[75] agreed with Spiegel that the composition of the parent alkaloid was represented by $C_{22}H_{28}O_3N_2$, but they believed that yohimboaic acid could best be regarded as $C_{21}H_{26}O_3N_2$, whereas Spiegel[76] contends that yohimbine is the *N*-methyl ester of yohimboaic acid, and should therefore have the composition $C_{20}H_{24}O_3N_2$. He rests his dissension from Barger and Field's conclusions on the ground that the barium salt chosen by them for analysis was not a suitable substance for examination.

Further light has been thrown on the constitution by a study of an intermediate compound formed from yohimbine and capable of conversion into yohimboaic acid.[76] This substance is produced when yohimbine is heated with half a molecule of dilute alcoholic potassium hydroxide. Further hydrolysis converts it into yohimboaic acid. This intermediate substance occurs free in technical yohimbine, from which it can be isolated by crystallisation from 50 per cent. alcohol. It is dextrorotatory, gives a crystalline hydrochloride, and contains a methoxyl group.

Attempts to apply the Hofmann reaction to yohimbine have been unsuccessful,[77] but the results are not without interest. When yohimbine methiodide is treated with potassium hydroxide, methylamine is liberated, whilst with silver oxide the methiodide is oxidised if the reaction is carried out in the presence of light. In the dark, silver oxide acts on the methiodide in cold methylalcoholic solution, with the production of methylyohimboaic acid. From this it follows that the methyl group in this last acid is attached to a nitrogen atom which, in yohimbine itself, is free, and in this way it is clear why attempts to prepare yohimbine by esterifying the acid have always proved fruitless.

The results of investigations of the constitution of yohimbine have not thrown light on its actual structure as yet, but the data which are being accumulated certainly give cause for hope that this

[73] E. Fourneau and H. J. Page, *Bull. Sci. Pharmacol.*, 1914, **21**, 7; *A.*, 1914, i, 862.

[74] L. Spiegel, *Ber.*, 1915, **48**, 2084; *A.*, 1916, i, 287.

[75] G. Barger and (Miss) E. Field, *T.*, 1915, **107**, 1025.

[76] L. Spiegel, *Ber.*, 1915, **48**, 2077; *A.*, 1916, i, 286.

[77] L. Spiegel and M. Corell, *ibid.*, 1916, **49**, 1086; *A.*, i, 667.

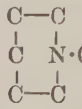
valuable compound may at no very far-off date be within the scope of synthetic chemistry.

Scopoline.

This alkaloid has been the subject of three papers during the last twelve months, but, as seems customary in the case of alkaloid chemistry, one of these is concerned chiefly with claims as to priority. The other two papers deal with the subject from different points of view, and apparently they support each other.

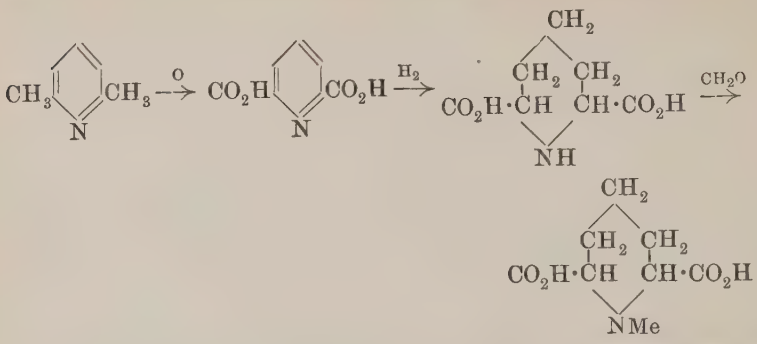
It appears probable that the constitution of scopoline may be represented by the formula C_7H_9,NMe,OH,O:, which, after all, does not lead us very far. An attempt[78] has been made to throw some light on the group C_7H_9. The oxidation of scopoline itself did not seem to lead far in this direction, but since scopoline can be quantitatively converted into norscopoline[79] by potassium permanganate, the nor-compound was used instead of the parent substance. An attempt to utilise the new method of oxidation by means of formaldehyde (see p. 141) failed, as norscopoline simply regenerates scopoline when submitted to this process. The deduction drawn from this was that scopoline contains a tertiary hydroxyl radicle. Scopolyl chloride also yielded negative results.

Scopoline was therefore heated in a sealed tube with hydrogen bromide in glacial acetic acid, and in this way a hydrobromide was formed which is easily reduced to a hydroscopoline. Oxidation of the latter compound produced 1-methylpiperidine-2:6-dicarboxylic acid (scopolic acid). This reaction gives the positions of all the carbon atoms in scopoline, and proves that the alkaloid is a piperidine derivative having the skeleton shown below:

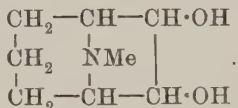


The proof of the constitution of scopolic acid was obtained by the synthesis of the compound in the following manner.[80] Lutidine was oxidised with potassium permanganate to lutidinic acid, which was then reduced by the Paal-Skita method (hydrogen and colloidal platinum) to hexahydro-2:6-lutidinic acid. The hydrochloride of this, when heated with formaldehyde solution at 135° for four hours, gave 1-methylpiperidine-2:6-dicarboxylic acid.

[78] K. Hess and A. Suchier, *Ber.*, 1915, **48**, 2057; *A.*, 1916, i, 285.
[79] *Ibid.*, 1886; *A.*, 1916, i, 67.
[80] K. Hess and F. Wissing, *ibid.*, 1907; *A.*, 1916, i, 74.



Another worker[81] has arrived at similar conclusions on the scopoline question, and suggests that the formula for hydroscopoline may be



Hydroscopoline ?

If these views should prove correct, the elucidation of the scopoline constitution is almost achieved.

For the disconnected nature of the present survey the Reporter has already offered his apologies, but, in conclusion, he feels it desirable to point out that this disconnectedness has had its advantages also, for it reproduces to some extent the impression which is derived from a study of the literature of the year, and so it serves to mirror the general trend of things in this branch of chemistry better, perhaps, than could have been done by a more detailed survey of restricted fields. Reports of the progress in the Heterocyclic Division are almost necessarily less interesting than those which deal with the other two sections of the subject. In the aliphatic and homocyclic series, test cases are found for new theories as well as for the study of chemical constitution, but in the heterocyclic group the main interest is confined to the investigations of molecular structure and the application of new methods of synthesis or degradation. Thus one of the most interesting features of organic chemistry is, generally speaking, absent from this Report, although in the current year it has been possible to deal with a theoretical problem in connexion with Friend's views on the metalammines.

A. W. Stewart.

[81] E. Schmidt, *Arch. Pharm.*, 1916, **253**, 497; *A.*, i, 285; see also *Ber.*, 1916, **49**, 164; *A.*, i, 419.

ANALYTICAL CHEMISTRY.

An immediate, and to some extent unforeseen, consequence of the war was the failure of a supply of glass suitable for laboratory vessels and of paper of the necessary quality for filter-paper for analytical purposes. Both difficulties have now been overcome. The formulæ for manufacturing glass of the right composition for every description of chemical apparatus were worked out last year,[1] and filter-papers of all types are now obtainable. The quality of the British filter-paper is quite equal, and in some cases superior, to that of its predecessor, for the necessity of supplying this want has caused special attention to be directed to the physical characteristics of good filter-paper, and the nature and origin of the impurities likely to be present.[2] For a moderately rapid paper, what is technically known as the "bulk," or, in other words, the ratio of the volume of the paper to that of the fibre, should be about 3·5 to 1, and as a rule it varies from 3—4·5 to 1. The occurrence of pinholes, which are sometimes to be found in paper of this bulk, is attributable to faults in the milling.

Physical Methods.

Increasing attention is being given to the utilisation of the physical characters of chemical substances as proofs of identity, and methods which until comparatively recently were only used empirically in restricted directions are now being more generally employed in analytical work.

This is particularly the case with the determination of the viscosity, which was for many years confined to the examination of oils by means of standard instruments. No special precautions were taken to eliminate the numerous sources of error, and the results obtained with one kind of instrument were not comparable with those obtained with another.

The adoption of a general method of expressing the viscosity of a liquid in absolute units would obviate these drawbacks, and with this end in view various formulæ have been worked out for

[1] *Proc. Inst. Chem.*, 1915, ii, 33.

[2] E. J. Bevan and W. Bacon, *Analyst*, 1916, **40**, 159.

calculating the measurements given by one standard instrument into those of another, and for expressing the results in terms of absolute viscosity.

For example, Ostwald's viscometer has been standardised by determining the efflux velocity of sulphuric acid from the capillary tubes at 25°.[3] The specific gravity and the percentage strength of the acid gave the required data for obtaining the viscosity by reference to the graph.[4] The absolute viscosity (η) was calculated by means of the formula $\eta = Kdt$, where d represented the specific gravity, t the efflux velocity in seconds, and K a constant depending on the size of the capillary tube of the particular instrument. In the case of Redwood's viscometer it was found that the relationship between the efflux velocity and the absolute viscosity could be expressed by means of a straight-line graph.

It is a general practice in commercial work to ignore the specific gravity of the liquid in viscosity measurements, but this may lead to considerable error.[5] The results may be corrected by multiplying the viscosity measurement by the specific gravity of the liquid at the temperature of the determination compared with that of water at 4°. Another source of error is the erroneous assumption that the average pressure in the instrument is exactly the mean of the initial and final pressures. To obviate this, a method of calculating the true average pressure has been devised.[6] The necessary correction to be applied for the loss of kinetic energy when a liquid issues from a capillary tube of uniform diameter, with its ends at right angles to its axis, has been ascertained, but it has yet to be determined whether the same correction is applicable to a capillary tube with a funnel-shaped opening. Pending this investigation, it is advisable not to use the latter form of tube.[7]

In view of the practical inconvenience attending the use of the present unit of absolute viscosity, the question of the advisability of employing a unit of lower value has again been raised. There is much to be said in favour of the proposal to term the viscosity unit the "poise" (after Poisseuille), with the "centipoise" ($1cp = 0{\cdot}01p$) as the practical unit of measurement. This value would be practically the same as the specific gravity of water at 20°, and on this basis the viscosity of an oil expressed in centipoises would be the same as its specific viscosity at that temperature.[8]

[3] C. A. Savill and A. W. Cox, *J. Soc. Chem. Ind.*, 1916, **35**, 151.
[4] A. E. Dunstan, *P.*, 1914, **30**, 105.
[5] P. C. McIlhiney, *J. Ind. Eng. Chem.*, 1916, **8**, 433.
[6] E. C. Bingham, H. I. Schlesinger and A. B. Coleman, *J. Amer. Chem. Soc.*, 1916, **38**, 27; *A.*, ii, 221.
[7] E. C. Bingham, H. I. Schlesinger, and A. B Coleman, *loc. cit.*
[8] P. C. McIlhiney, *loc. cit.*

The chief contribution to the applications of the spectroscope in analytical work has been an investigation of the differences in the spectra of the alkali salts of the phthaleins of different phenols. These show distinctive absorption bands, the different positions of which afford the means of identifying the various phenols.[9]

Reference may also be directed to an important paper dealing with the methods of measuring absorption spectra and comparing the wave-lengths with those of a standard pure substance of known composition.[10]

The measurement of the optical dispersion has now become a standard method for testing the purity of Chinese wood oil. The method has been simplified by placing the oil in a hollow prism in the spectrometer and taking a direct reading of the dispersion by means of an arc light. The relative dispersion for two lines given by this light in the red and blue parts of the spectrum is determined, and from the difference between the angular measurements given by Chinese wood oil and its principal adulterants, the degree of purity of the sample may be rapidly ascertained.[11]

Gas Analysis.

The systematic study of the different reagents used or suggested for use in the analysis of mixtures of gases has been continued from last year,[12] especially by American chemists, and several papers giving details of considerable value have been published.

Some of the reagents which have, in recent years, been proposed for the separation of individual constituents of gaseous mixtures have little to recommend them beyond their novelty, whilst others have not fulfilled the expectations of their proposers. For example, the use of a solution of phosphorus in castor oil, which Centnerszwer [13] suggested for the absorption of oxygen, is quite unsuitable for the purpose.[14] At the ordinary temperature the absorption of the gas is incomplete, which may possibly be due to the oil only retaining a small amount of phosphorus in solution. It is conceivable that by the use of a hot solution of phosphorus in oil complete absorption of oxygen might be effected, but such a reagent would not be altogether easy to manipulate, and even assuming that, under such conditions, it gave quantitative results, it would not

[9] H. Gsell, *Zeitsch. anal. Chem.*, 1916, **55**, 417; *A.*, ii, 584.
[10] F. Weigert, *Ber.*, 1916, **49**, 1496; *A.*, ii, 545.
[11] E. E. Ware, *J. Ind. Eng. Chem.*, 1916, **8**, 126.
[12] R. P. Anderson, *J. Ind. Eng. Chem.*, 1915, **7**, 587; *A.*, 1915, ii, 647.
[13] M. Centnerszwer, *Chem. Zeit.*, 1910, **34**, 494; *A.*, 1910, ii, 541.
[14] R. P. Anderson and W. Biederman, *J. Ind. Eng. Chem.*, 1916, **8**, 135; *A.*, ii, 262.

offer any advantage over the ordinary method of absorption with alkaline pyrogallol.

Chromous chloride solution is a much more promising reagent, but so far it, too, has failed to justify the claim that it could advantageously replace alkaline pyrogallol.[15] Unfortunately, solutions of chromous chloride prepared in the usual way by the interaction of chromous acetate and hydrochloric acid are unstable, and gradually decompose, with the liberation of hydrogen, thus rendering analytical results untrustworthy. On the other hand, a solution of chromous chloride prepared by reducing violet chromic chloride with hydrogen at 400—500° and filtering the liquid through glass wool, is a stable reagent, but does not absorb oxygen completely. Although the conditions for preparing a satisfactory stable solution might be established, the cost of the materials and the trouble of preparing it would probably prevent its general adoption in gas analysis, notwithstanding the fact that the presence of carbon dioxide or hydrogen sulphide does not interfere with the absorption of oxygen by chromous chloride.

For use with a viscous solution of potassium pyrogallol, which has been found a more efficient absorption reagent than weaker solutions,[16] Orsat's original pipette gives better results than the other forms of pipette devised as improvements on that instrument, for the absorption of oxygen by weak solutions, without shaking. It is quite effective for the absorption of oxygen from the air, but for the analysis of gases rich in oxygen, shaking is required, and a modification of Orsat's pipette has been designed to prevent obstructions caused by the formation of precipitates.[18] The modified pipette has a conical top, and the glass tubes are supported on a cone of perforated porcelain.

Solutions of sodium pyrogallol have been found to absorb oxygen more rapidly than any solution of potassium pyrogallol, complete absorption being effected within four minutes.[19] A solution which has five times the absorptive capacity of Anderson's most effective potassium pyrogallol reagent[20] consists of sodium hydroxide, pyrogallol, and water in proportions of 7·36 : 10·0 : 11·62 by weight. A solution of this description is too concentrated for any carbon monoxide to be liberated on contact with oxygen, although

[15] R. P. Anderson and J. Riffe, *J. Ind. Eng. Chem.*, 1916, **8**, 24; *A.*, ii, 261.

[16] R. P. Anderson, *ibid.*, 1915, **7**, 587; *A.*, 1915, ii, 647.

[17] R. P. Anderson, *ibid.*, 1916, **8**, 131; *A.*, ii, 262.

[18] R. P. Anderson, *ibid.*, 133; *A.*, ii, 262.

[19] J. W. Shipley, *J. Amer. Chem. Soc.*, 1916, **38**, 1687; *A.*, ii, 571.

[20] R. P. Anderson, *J. Ind. Eng. Chem.*, 1915, **7**, 587; *A.*, 1915, ii, 647.

it has been established[21] that dilute solutions of sodium hydroxide will evolve carbon monoxide under these conditions.

Attention has been directed[22] to a source of error in the analysis of generator gas through incomplete absorption of carbon monoxide by ammoniacal cuprous chloride, and the combustion method is therefore more trustworthy for the estimation of hydrogen, methane, and carbon monoxide in such gases. The method of fractional combustion with copper oxide[23] has been shown to yield accurate results with gaseous mixtures of all kinds.[24] The most suitable temperature for the combustion is 275—300°.

As direct methods, when practicable, are more satisfactory than indirect methods, a new process of estimating carbon monoxide in the presence of unsaturated hydrocarbons seems worthy of thorough investigation.[25] It is based on the fact that when a gaseous mixture is repeatedly passed through a tube charged with soda-lime (containing about 20 per cent. of sodium hydroxide) heated at 230°, any carbon monoxide present is absorbed and retained by the soda-lime. Obviously, the gas must first be freed from carbon dioxide and oxygen by being passed through absorption pipettes charged with the usual reagents. The method appears to be capable of general application, and should further investigation confirm its trustworthiness, it should find a permanent place in schemes for the analysis of gases.

A rapid and accurate process of estimating sulphur in small quantities of coal gas has been based on its oxidation by combustion with an excess of air in a quartz tube containing platinum in the form of gauze and wire fabric.[26] The most efficient reagent for absorbing sulphur compounds in gas is phenylhydrazine. The combustion test in the presence of porous platinum may also be used for the detection of sulphur in 10 c.c. of gas.

A colorimetric method of estimating acetylene has been devised by two chemists, apparently working independently of each other.[27] Essentially it consists in passing the gas through an ammoniacal solution of cuprous chloride to which gelatin has been added to prevent the subsidence of the resulting cuprous acetylide. The red colour produced is compared with standard colours, which

[21] V. B. Lewes, *J Soc. Chem. Ind.*, 1891, **10**, 407.

[22] F. Hoffmann, *Chem. Zeit.*, 1916, **40**, 412; *A.*, ii, 395.

[23] G. von Knorre, *ibid.*, 1909, **33**, 717; *A.*, 1909, ii, 698.

[24] G. A. Burrell and G. G. Oberfell, *J. Ind. Eng. Chem.*, 1916, **8**, 228; *A.*, ii, 260.

[25] A. Pivá, *Ann. Chim. Applicata*, 1916, **5**, 82; *A.*, ii, 343.

[26] F. Mylius and C. Hüttner, *Ber.*, 1916, **49**, 1428; *A.*, ii, 571

[27] E. R. Weaver, *J. Amer. Chem. Soc.*, 1916, **38**, 352; *A.*, ii, 275; A. Schulze, *Zeitsch. angew. Chem.*, 1916, **29**, i, 341; *A.*, ii, 649.

may be prepared from a solution of a red dyestuff suitably diluted, or may consist of standard red glasses. The method is capable of detecting 0·03 mg. of acetylene and of estimating quantities up to 2·0 mg., but it is essential that, prior to the test, the gas should be freed from hydrogen sulphide or notable quantities of oxygen or carbon dioxide.

In connexion with the subject of gas analysis, reference may be made to a form of apparatus designed for the examination of minute quantities of gases.[28]

Agricultural Analysis.

The limitation in the supply of phosphates, due to the war, has caused special attention to be paid to the methods of estimating the value of phosphatic manures for agricultural purposes, and it is not surprising that criticisms should have been directed against the methods of estimation commonly employed.

In the early part of the year a paper was published[29] giving details of experiments on mineral phosphates of various origin, and it was shown that from 90 to 100 per cent. of their phosphoric acid could be dissolved by 2 per cent. citric acid solution provided that a sufficient number of extractions were made. Free lime or calcium carbonate causes a pronounced reduction in the solubility—so much so that in the presence of much calcium carbonate the citric acid test as ordinarily applied is a measure of the calcium rather than of the phosphoric acid. On the other hand, the greater the proportion of calcium in combination with the phosphoric acid the greater is the solubility. The results of the test are also affected by the degree of fineness to which the mineral has been ground, whilst calcining progressively reduces the solubility. From the results of these experiments it would seem that the citric acid test must be regarded as of no value as a criterion of the relative suitability of phosphatic fertilisers for plant life, and that there is no reason why mineral phosphates should not give as good results as basic slag in agriculture.

Even when used for the evaluation of basic slag, the citric acid method may yield fallacious results if the slag has been produced by the use of fluorspar.[30] In the case of such slags there is no definite ratio between the amounts of silica and dissolved phosphoric acid, whereas in the case of slag readily soluble in citric acid the ratio between the two constituents is fairly constant.

[28] P. A. Guye and F. E. E. Germann, *J. Chim. phys.*, 1916, **14**, 195; *A.*, ii, 445.

[29] G. S. Robertson, *J. Soc. Chem. Ind.*, 1916, **35**, 217; *A.*, ii, 196.

[30] *Ibid.*, 216; *A.*, ii, 196.

Hence it would appear that in fluor spar slags the silica is not in combination with the phosphoric acid. Such slags resemble mineral phosphates in yielding the whole of their phosphoric acid to citric acid solution if sufficient time be allowed for solution, but their behaviour affords a further proof that the citric acid test cannot be trusted as a criterion of the agricultural value of phosphates.

The test has become so firmly established, however, that it is unlikely to be discarded, at any rate for the analysis of ordinary basic slags. In fact, several modifications of the method have been described during the past year, most of them having as their main object the more efficient prevention of the interference of silica when present in large amounts.

It has been shown[31] that in the iron citrate method[32] there is always sufficient iron present in the iron citrate, even when prepared from ferric chloride poor in iron, to prevent the interference of silica. The addition of too great a quantity of hydrogen peroxide causes the results to be too low, possibly owing to the influence of the silica. Both ferric chloride solution and hydrogen peroxide should have been recently prepared, and the reagents should be added in the following order: (1) iron citrate; (2) hydrogen peroxide; and (3) magnesium oxide.[33]

In a modification of the citro-uranium method,[34] the phosphoric acid is precipitated as ammonium magnesium phosphate,[35] the precipitate dissolved in acetic acid, and the solution titrated with uranium acetate, with potassium ferrocyanide as indicator. The influence of silica is inhibited by boiling the solution with ferrous sulphate and filtering it from the resulting precipitate.

A new method of estimating the phosphoric acid insoluble in citric acid solution has been based on the establishment of a definite relationship between the amounts of phosphoric acid precipitated by ammonia and the citrate-insoluble phosphoric acid. By dividing the amount of phosphoric acid in the precipitate by the factor 1·5, the amount of phosphoric acid insoluble in citric acid solution is obtained.[36]

For the estimation of phosphorus in soil several good methods are available, and comparative experiments have shown that con-

[31] M. Popp, *Chem. Zeit.*, 1916, **40**, 257, ii, *A*; ii, 266.

[32] *Ibid.*, 1912, **36**, 937; *A.*, 1912, ii, 992; *Landw. Versuchs-Stat.*, 1913, **79**, 229, 465; *A.*, 1913, ii, 306, 876; *Chem. Zeit.*, 1914, **38**, 741; *A.*, 1914, ii, 576.

[33] Celichowski and F. Pilz, *Zeitsch. landw. Vers-Wesen Oesterr.*, 1915, **18**, 581; *A.*, ii, 342.

[34] D. Crispo and R. W. Tuinzing, *Landw. Versuchs-Stat.*, 1916, **88**, 131; *A.*, ii, 342.

[35] Popp, *loc. cit.*

[36] C. H. Hunt, *J. Ind. Eng. Chem.*, 1916, **8**, 251; *A.*, ii, 265.

cordant results may be obtained either by fusion with alkalis, by Washington's method of treatment with hydrofluoric and nitric acids, or by Fisher's aqua regia method.[37] The presence of titanium or tungsten in the soil does not affect the accuracy of the results, but vanadium should be eliminated by a method such as that of Cain and Tucker.[38] It is necessary to take into account, however, that treatment with hydrofluoric acid or ammonium fluoride may cause a loss, on subsequent ignition, of phosphorus as phosphorus fluoride. The loss is slight in the case of alkali metals, but considerable with phosphates of alkaline earth metals.[39]

A rapid method of estimating calcium oxide in peat soils consists in treating the soil with aqua regia, evaporating the mixture to dryness, extracting the residue with dilute acid, and precipitating the calcium as oxalate, after previous separation of iron and aluminium. The precipitate is washed, treated with concentrated sulphuric acid, and titrated with standard permanganate. The method is not applicable to soils containing much mineral matter.[40]

Test estimations of the carbonates in soil by absorbing the evolved carbon dioxide in barium hydroxide, as in Marr's method,[41] and titrating the resulting barium carbonate, as described by Cain,[42] have shown that the method may be accepted as trustworthy.[43]

Organic Analysis.

Qualitative.—It is only to a limited extent that it has been found possible to establish group reagents in organic chemistry, for in many cases a reaction can only be regarded as distinctive of a certain class of compounds when other classes are known to be absent.

For example, the blue coloration with characteristic spectrum which "ninhydrin" gives with amino-acids[44] is only specific when certain conditions as to temperature and concentration are observed. All ammonium salts give the same reaction in a slightly alkaline solution,[45] and hence other bases which yield ammonia or are readily oxidisable might be mistaken for amino-acids.[46]

[37] W. O. Robinson, *J. Ind. Eng. Chem.*, 1916, **8**, 148; *A.*, ii, 265.
[38] J. R. Cain and F. H. Tucker, *ibid.*, 1913, **5**, 647; *A.*, 1913, ii, 875.
[39] A. Davis and J. A. Prescott, *J. Agric. Sci.*, 1916, **8**, 136.
[40] R. A. Gortner, *Soil Sci.*, 1916, **1**, 505; *A.*, ii, 449.
[41] F. S. Marr, *J. Agric. Sci.*, 1909, **3**, 155; *A.*, 1909, ii, 938.
[42] J. R. Cain, *J. Ind. Eng. Chem.*, 1914, **6**, 465; *A.*, 1914, ii, 577.
[43] C. J. Schollenberger, *ibid.*, 1916, **8**, 427; *A.*, ii, 395.
[44] S. Ruhemann, *T.*, 1910, **97**, 2025.
[45] V. J. Harding and F. H. S. Warneford, *J. Biol. Chem.*, 1916, **25**, 319; *A.*, ii, 459. [46] V. J. Harding and R. M. MacLean, *ibid.*, 337; *A.*, ii, 459.

Again, a general reaction for alkaloids containing a phenolic group (morphine, etc.) has been based on the coloration which most phenols give with a solution of titanium trioxide in presence of sulphuric acid,[47] the colour ranging from blood-red to orange in the case of different alkaloids. Here, too, the distinctive nature of the test is weakened by the fact that proteins containing a tyrosine group give a similar coloration.[48]

A useful test for distinguishing between aromatic and aliphatic aldehydes has been based on the different behaviour of the classes of compounds on treatment with a chloroform solution of acenaphthene in the presence of sulphuric acid. Aromatic aldehydes yield a green ring, changing to reddish-violet, at the zone of separation, or, if the liquid be shaken, it becomes first green and then reddish-violet, whilst aliphatic aldehydes yield black or dark green condensation products. The colour reaction, which is very sensitive, is also given by aldoses and carbohydrates which yield formaldehyde or a similar aldehyde when treated with cold sulphuric acid.[49]

A new reaction for the detection of picric acid is based on the formation of 2-bromo-4 : 6-dinitrophenol. This gives a red coloration with ammonia vapour or potassium cyanide, and the test is fairly sensitive, being capable of detecting 5 mg. of picric acid in a litre of beer or urine.[50]

A study of the various methods of detecting hydrocyanic acid has shown that the guaiacum–copper sulphate test is capable of detecting 0·00039 mg. of cyanogen in 10 c.c. of solution, whilst the silver cyanide test and the method of converting the cyanogen into thiocyanate are not sensitive to less than ten times that amount.[51]

A test for glycerol depending on the coloration given by its vapours with a reagent consisting of magenta, sulphurous acid, and sulphuric acid[52] has now been modified so as to be capable of detecting glycerides in the presence of hydrocarbons, waxes, etc. Under the prescribed conditions, the vapours from glycerides give a red coloration, changing to blue on heating, whilst the vapours from resins, waxes, etc., give a red coloration, which becomes colourless when heated.[53]

[47] Compare O. Hauser and A. Lewite; *Ber.*, 1912, **45**, 2480; *A.*, 1912, i, 847.

[48] G. Denigès, *Bull. Soc. chim.*, 1916, [iv], **19**, 308; *A.*, ii, 544.

[49] R. de Fazi, *Gazzetta*, 1916, **46**, i, 334; *A.*, ii, 457.

[50] J. Castets, *J. Pharm. Chim.*, 1916, [vii], **13**, 46; *A.*, ii, 160.

[51] G. Anderson, *Zeitsch. anal. Chem.*, 1916, **55**, 459; *A.*, ii, 585.

[52] M. François and E. Boismenu, *J. Pharm. Chim.*, 1915, [vii], **11**, 49; *A.*, 1915, ii, 110.

[53] M. François, *ibid.*, 1916, [vii], **13**, 65; *A.*, ii, 155.

A test for detecting formic acid in acetic acid and vinegar, which is based on its reducing action on chromic acid,[54] suffers from the same drawbacks as similar tests previously suggested. Reduction is caused not only by formic acid, but also by other constituents normally present in wine and grain vinegars, and the test cannot be regarded as absolutely conclusive even in the case of commercial acetic acid.

An illustration of the way in which a colour reaction may be misleading is afforded by the fact that Japanese soja beans contain a constituent which gives a violet coloration with ferric chloride.[55] This might easily be mistaken for salicylic acid, but, unlike that acid, it does not give a coloration with Millon's or Jorissen's reagents. The last-named reagent should therefore be used in testing for salicylic acid in beans.

Of the various tests proposed for distinguishing between gum arabic and other gums and dextrins, the reaction given by basic lead acetate is the most distinctive. As confirmatory tests, a copper reagent prepared by mixing copper sulphate with sodium hydroxide, and a reagent consisting of a mixture of ferric chloride and alcohol, may be used.[56]

Quantitative.—There have been few contributions to the methods of elementary analysis during the past year. The most important, perhaps, is the adaptation of the chromic acid method of combustion[57] to the simultaneous estimation of carbon and halogens in organic compounds, the modification being also applicable to the estimation of carbon alone in substances the combustion of which is difficult by the ordinary method.[58]

To effect complete combustion of traces of carbon monoxide, a silica tube containing platinised asbestos is connected with the outlet of the reaction flask, whilst oxides of sulphur are absorbed in a U-tube packed with glass wool moistened with sulphuric acid. During the combustion, a current of oxygen is passed through the apparatus. When the method is used for the estimation of carbon by itself, the resulting carbon dioxide may be estimated either gravimetrically or volumetrically. In the latter case, the gas is absorbed by standard baryta solution, the excess of which is subsequently titrated with acid. For the simultaneous estimation of carbon and bromine, the gaseous products are absorbed in tubes containing standard sodium hydroxide solution containing a little

[54] P. Szebényi, *Zeitsch. Nahr. Genussm.*, 1916, **31**, 16; *A.*, ii, 542.

[55] H. C. Brill, *Philippine J. Sci.*, 1916, **11**, 81.

[56] C. E. Waters and J. B. Tuttle, *J. Ind. Eng. Chem.*, 1916, **8**, 413; *A.*, ii, 400.

[57] P. W. Robertson, *T.*, 1915, **107**, 902.

[58] *Ibid.*, 1916, **109**, 215; *A.*, ii, 267.

standard sodium sulphite solution, and the contents subsequently treated with barium nitrate and filtered. The filtrate is titrated with standard nitric acid, and the bromine estimated volumetrically by the silver nitrate method. To obtain the amount of carbon dioxide, the value of the bromine is deducted from the total alkalimetric result. In the case of chlorine, a second heated silica tube is required to decompose any chromyl chloride and retain the chromium as chromium oxide. Estimation of nitrogen by Kjeldahl's method in the residue in the reaction flask gives unsatisfactory results.

A special form of combustion tube has been devised for the simultaneous estimation of carbon, hydrogen, and mercury in organic compounds,[59] the mercury being absorbed and weighed in a small inner tube containing gold leaf or a spiral of gold wire. The inlet of this tube is packed with calcined asbestos into a constricted portion of the combustion tube, and the escape of mercury vapour or water through the joints is prevented by the introduction of dry oxygen through a side tubulure in the outer tube at a pressure somewhat higher than that within the tube.

The chromic acid method of oxidation has also been found useful for estimating the carbon in the organic non-sugar constituents of sugar scums.[60]

Oxalic acid is frequently employed as an original standard in alkalimetry, and provided it is purified by recrystallisation, gives trustworthy results. For its titration with alkalis, with methyl-orange as indicator, it is advisable to add an equivalent quantity of calcium chloride before completing the neutralisation, so as to counteract the tendency to the formation of hydrogen alkali oxalates.[61] The iodometric method of Sander[62] is less accurate than titration with alkali.[63] Iodine is liberated with extreme slowness towards the end of the reaction, whilst the addition of calcium chloride causes the results to be too low.[61] For accuracy, the gravimetric method of precipitating the oxalic acid as calcium oxalate, and weighing the resulting calcium carbonate, is to be preferred to any volumetric process.[63]

A method of estimating alcohol in the presence of phenol consists in rendering the mixture strongly alkaline with sodium hydroxide, distilling part of the liquid, destroying any phenol in

[59] V. Grignard and A. Abelmann, *Bull. Soc. chim.*, 1916, [iv], **19**, 25; *A.*, ii, 149.

[60] V. Stanček, *Zeitsch. Zuckerind. Böhm.*, 1916, **40**, 201; *A.*, ii, 267.

[61] G. Bruhns, *Zeitsch. anal. Chem.*, 1916, **55**, 23; *A.*, ii, 158.

[62] A. Sander, *Zeitsch. angew. Chem.*, 1914, **27**, 192; *A.*, 1914, ii, 482.

[63] A. Blanchetière, *Bull. Soc. chim.*, 1916, [iv], **19**, 300; *A.*, ii, 543.

the distillate by means of bromine, the excess of which is removed by thiosulphate solution, and distilling off the alcohol.[64]

Messinger's method of estimating acetone in presence of ethyl alcohol,[65] which depends on its conversion into iodoform, has the drawback that iodoform is also produced from the alcohol in a proportion increasing with the temperature. This may be obviated by using baryta or lime-water to replace the potassium hydroxide. Under the specified conditions only a slight error, for which a correction may be made, is then introduced by the alcohol in mixtures containing 10 per cent. of acetone, but in the case of mixtures containing only about 1 per cent. the results are less trustworthy, since the necessary correction for the alcohol is too large in proportion to the acetone.[66]

For the estimation of paracetaldehyde and acetal in the presence of each other, advantage may be taken of the fact that they are decomposed at different rates when heated with dilute acids.[67] Acetal in 1 per cent. solution is rapidly hydrolysed when boiled with a strong acid of a concentration of $N/6000$, whereas paracetaldehyde is stable until the concentration is increased to $N/2000$, and is only rapidly hydrolysed when the concentration reaches $N/10$. In practice it is preferable to use an equivalent quantity of acetic acid in place of a strong acid. Acetaldehyde, if also present, is separated by a preliminary distillation, whilst the acetaldehyde resulting from the decomposition of the paracetaldehyde and acetal is distilled after each acid treatment. For its estimation either Ripper's hydrogen sulphite method or the neutral sulphite method of Seyewetz gives good results.

A convenient method of estimating ferro- and ferri-cyanides in the presence of cyanides and thiocyanates is based on the titration of the ferrocyanide, with titanium trichloride, after the addition of a large excess of ammonium thiocyanate. Alkalinity due to cyanides is neutralised with standard acid, while ferrocyanides are oxidised to ferricyanides by means of acid permanganate, or, if thiocyanates are also present, by means of iodine solution. The difference between the results of the titration with titanium trichloride before and after the oxidation corresponds with the ferrocyanide present. Soluble chlorides and sulphates do not interfere with the estimation unless present in combination with metals which form insoluble double ferrocyanides.[68]

[64] J. Ehrlich, *J. Ind. Eng. Chem.*, 1916, **8**, 240; *A.*, ii, 349.
[65] J. Messinger, *Ber.*, 1888, **21**, 3366; *A.*, 1889, ii, 313.
[66] J. Rakshit, *Analyst*, 1916, **41**, 245; *A.*, ii, 544.
[67] K. J. P. Orton and (Miss) P. V. McKie, *T.*, 1916, **109**, 184; *A.*, ii, 384.
[68] F. G. W. Knapman and E. L. Randall, *Chem. News*, 1916, **113**, 265; *A.*, ii, 501.

Another application of titanous chloride is in the estimation of substituted phenylhydrazines and *p*-nitrophenylhydrazones, which are quantitatively reduced by boiling with the reagent, whilst phenylhydrazine is unaffected. The excess of titanous chloride is subsequently titrated with standard crystal-scarlet solution.[69]

In the analysis of commercial benzols the toluene may be estimated by distilling the sample at a specified rate and measuring the quantity of distillate obtained up to 90°. Thence by reference to a curve the amount of toluene, within about 1 per cent., is obtained. Carbon disulphide is estimated from the difference in the specific gravity of the sample before and after removal of the disulphide by the addition of alcoholic potassium hydroxide. After removal of carbon disulphide as xanthate, the proportions of benzene, toluene, and paraffin in the residue are found from the differences between the observed and recorded specific gravities as given in a table.[70] The method is also applicable to benzol first runnings, even when containing a high proportion of carbon disulphide, but it is advisable to dilute the liquid with a definite amount of purified benzene before the distillation.[71] Another method of estimating benzene and toluene in commercial mixtures is to separate the constituents in pairs, benzene–toluene and toluene–xylene, by fractional distillation, and to obtain the composition of each mixture from the boiling points. Curves showing the relationship between the boiling points have been constructed from the respective vapour pressures and checked by the results obtained with mixtures of the pure substances.[72]

A new method of estimating phloroglucinol and resorcinol is based on the fact that they yield insoluble precipitates when treated, in hydrochloric acid solution, with furfuraldehyde. When obtained under constant conditions as to acidity, volume of liquid, etc., the precipitates stand in definite relationship to the quantities of these phenols, and may be washed, dried at 100—105°, and weighed. Phenol, quinol, toluquinol, and catechol do not form insoluble precipitates with the aldehyde, but cresols, xylenols, pyrogallol, orcinol, and diresorcinol are precipitated by it.[73]

Attention has been directed to sources of error in estimating dicyanodiamide in calcium cyanamide by Caro's method.[74] Precipitation of a small quantity of dicyanodiamide at the same time as

[69] F. Robinson, *J. Soc. Dyers*, 1916, **32**, 81 ; *A.*, ii, 355.

[70] P. E. Spielmann and E. G. Wheeler, *J. Soc. Chem. Ind.*, 1916, **35**, 396; *A.*, ii, 348.

[71] P. E. Spielmann and F. B. Jones, *ibid.*, 912 ; *A.*, ii, 583.

[72] A. Edwards, *ibid.*, 587 ; *A.*, ii, 452.

[73] E. Votoček and R. Potmešil, *Ber.*, 1916, **49**, 1185 ; *A.*, ii, 542.

[74] N. Caro, *Zeitsch. angew. Chem.*, 1910, **23**, 2407 ; *A.*, 1911, ii, 162.

the silver cyanamide cannot be prevented even by the addition of ammonia in excess, whilst slight decomposition of the dicyanodiamide takes place when the filtrate from the silver cyanamide is boiled with potassium hydroxide. Hence the results given by the method are too low, and the larger the proportion of dicyandiamide the greater will be the error.[75] It is preferable to precipitate the cyanamide with neutral silver nitrate, and to add the ammonia afterwards, and to estimate the dicyandiamide by precipitating it simultaneously with the cyanamide by means of silver nitrate and 2 per cent. potassium hydroxide solution, and estimating the nitrogen in the precipitate by Kjeldahl's method.[76]

A useful paper dealing with the analysis of carbohydrates by means of enzymes and special yeasts was published early in the year.[77] This gave a critical review of the various methods which have been proposed for the biological estimation of raffinose, maltose, and other sugars and starch, and described the most satisfactory means of obtaining active preparations of the enzymes from the specific micro-organisms. Incidentally, it is shown by experiments that reducing sugars are not actually precipitated by basic lead acetate, but that lævulose, for example, is either destroyed by the lead salt or it is transformed into another sugar with a different specific rotatory power and a smaller reducing power. Hence in sugar analysis any considerable excess of basic lead acetate should be avoided, and such excess should be removed before polarisation.

No loss of lævulose occurs, however, unless the excess of lead is allowed to act on the sugar for some time before being precipitated.[78]

In estimating reducing sugars in the presence of a large excess of sucrose it is essential to take into account such factors as the temperature and the duration of heating, and to vary the amounts of sugar taken for the analysis according to the temperature and the proportion of invert-sugar present.[78a]

In the case of products containing much invert-sugar, the cuprous oxide method of estimation is preferable, whilst for those poor in invert-sugar the thiosulphate method gives the best results.

The most suitable temperature for estimating the reducing power of invert-sugar in presence of sucrose is 65°, since at that temperature the reducing capacity of sucrose is negligible, whereas at higher

[75] G. Hager and J. Kern, *Zeitsch. angew. Chem.*, 1916, **29**, 309; *A.*, ii, 587.

[76] E. Truniger, *Schweiz. Ver. anal. Chem.*, May 26 and 27, 1916.

[77] W. A. Davis, *J. Soc. Chem. Ind.*, 1916, **35**, 201; *A.*, ii, 202.

[78] W. A. Davis, *J. Agric. Sci.*, 1916, **8**, 7.

[78a] L. Maquenne, *Compt. rend.*, 1916, **162**, 207; *A.*, ii, 156.

temperatures, particularly from 90° to 100°, there is a pronounced increase in the reduction.[79]

Industrial sugars contain reducing sugars other than invert-sugar, and these resemble sucrose in showing a greater cupric reducing power at boiling point (103—104°) than at 65°; whereas in the case of invert-sugar there is only a slight increase in the reducing power on raising the temperature from 65° to boiling point. Hence by estimating the difference in the reduction caused by the industrial sugar at the two temperatures, in comparison with that caused by sucrose, it is possible to form an approximate conclusion as to the amount of these unknown sugars in the product.[80]

An experimental investigation of the method of estimating pentoses and pentosans by means of Fehling's solution[81] has shown that the modification devised by L. Eynon and J. H. Lane[82] is trustworthy, but it is suggested that by making two alterations in the procedure, sources of error would be obviated: (1) by using a larger proportion of the distillate with a correspondingly greater amount of Fehling's solution, a greater weight of copper oxide is obtained, and errors due to multiplication are reduced; (2) by immersing the flask in a boiling-water bath, instead of boiling the solution, the reduction of Fehling's solution in the "blank" test is diminished by more than three-quarters. The large, spontaneous reduction which occurs when the Fehling's solution containing the salt derived from the neutralisation of the acid is boiled alone, is probably due to the higher boiling point of the mixture. The reduction due to the furfuraldehyde is not affected by the presence of the salt, but the amount of copper oxide to be deducted from the total obtained when the solution is boiled is inconveniently large.[83]

Most of the contributions to the analysis of oils and fats have dealt with the physical and chemical characters of less known products, and there have been few additions to the known methods of examination.

It has long been known that a definite relationship exists between some of the constants of fats, and a formula has now been established which includes the refractive index, n, specific gravity, d, saponification value, V, and iodine value, I:—

$$\frac{n^2t-1}{n^2t+2} \times \frac{100}{d_{\frac{t}{4}}^{t}} = 33{\cdot}07 + 0{\cdot}00075I - 0{\cdot}01375V + 0{\cdot}002\,(t-15).$$

In the presence of hydroxy-acids the first figure of the equation

[79] L. Maquenne, *Compt. rend.*, 1916, **162**, 145; *A.*, ii, 156.
[80] *Ibid.*, 277; *A.*, ii, 202.
[81] J. T. Flohill, *Chem. Weekblad*, 1910, **7**, 1057.
[82] *Analyst*, 1912, **37**, 41; *A.*, 1912, ii, 305.
[83] J. L. Baker and H. F. E. Hulton, *ibid.*, 1916, **41**, 294; *A.*, ii, 651.

is lower. The relationship also holds good for hydrogenated oils.[84]

A method for estimating the degree of rancidity of oils and fats is based on the proportion of aldehydes, etc., liberated on distillation in a current of steam under constant conditions, and measured by titration with permanganate solution. The difference between the amount of permanganate required for the oxidation and that consumed in a blank test gives the *oxidisability value*, which may be defined as the mg. of oxygen required to oxidise the volatile organic compounds separated under constant conditions from the fat.[85]

Speaking generally, the oxidisability value of sound, fresh fats varies from about 3 to 10, whilst rancid fats may show values up to 50 or higher. There is no definite relationship between the acid value and the oxidisability value.

The bromine thermal value[86] affords a rapid method of estimating the iodine value of most unoxidised oils. In a recent modification of the method[87] the heat of bromination is expressed in calories per gram of oil, and the relationship of the values to the iodine values of a number of typical oils is given. Any pronounced differences between the calculated and determined iodine values must be attributed to there being a greater amount of substitution by the bromine than by the iodine.

Estimation of the stearic acid in fatty acids by crystallisation from a saturated alcoholic solution of pure stearic acid[88] sometimes gives abnormal results. These have been found to be due to supersaturation, as a result of insufficient stearic acid in the solution, and the error due to this cause may be prevented by adding a known quantity of pure stearic acid in excess of that required to saturate the alcohol, and deducting the weight of the deposit obtained in a "blank" experiment from that recovered in the actual estimation.[89]

A rapid method of estimating glycerol as sodium glyceroxide in oils gives results in agreement with the amount of glycerol calculated from the ester value, provided that any free fatty acids in the oil are removed before the treatment with sodium ethoxide solution and light petroleum.[90]

[84] H. J. Backer, *Chem. Weekblad*, 1916, **35**, 954; *A.*, ii, 543.
[85] G. Issoglio, *Ann. Chim. Applicata*, 1916, **6**, 1; *A.*, ii, 401.
[86] O. Hehner and C. A. Mitchell, *Analyst*, 1895, **20**, 148.
[87] J. W. Marden, *J. Ind. Eng. Chem.*, 1916, **8**, 121.
[88] O. Hehner and C. A. Mitchell, *Analyst*, 1896, **21**, 316.
[89] E. B. Holland, J. C. Reed, and J. P. Buckley, jun., *J. Agric. Research*, 1916, **6**, 101.
[90] H. Bull, *Chem. Zeit.*, 1916, **40**, 690; *A.*, ii, 584.

The digitonin method of separating cholesterol and phytosterol is more trustworthy than the older method, and has the advantage that it can in most cases be applied, at all events as a qualitative test, to the fats themselves. For a quantitative estimation it is preferable to apply the reagent to the separated fatty acids. Even for the estimation of cholesterol in blood, precipitation with digitonin is more accurate than the colorimetric method.[91]

A new method of separating and estimating cholesterol and *iso*cholesterol has been based on the precipitation of the former by means of oxalic acid, and of the latter in the filtrate as a benzoate.[92]

A method of estimating alkaloids as hydrochlorides is more simple than many of the standard methods, while yielding equally accurate results. The alkaloid is extracted with ether, hydrogen chloride passed through the ethereal solution, the solvent evaporated, and the residual hydrochloride weighed; or the residue may be dissolvd in water, and the solution titrated with standard alkali solution. With suitable modifications for the extraction, the method gives trustworthy results in the estimation of alkaloids in such products as conium seeds, colchicum root, and tobacco.[93]

A critical examination of the methods of estimating nicotine in tobacco[94] has shown that precipitation of the alkaloid by means of silicotungstic acid[95] is trustworthy, and a simpler modification has been suggested. Pyridine, which causes the results to be too high, is best separated from the nicotine by distillation with steam from an acetic acid solution, which retains the nicotine. Accurate results may be obtained by the methods of Kissling[96] and of Koenig,[97] but the methods of Keller[98] and of Tóth[99] are not so trustworthy, and Ulex's[1] method is untrustworthy. Thoms'[2] method of precipitation by a potassium–bismuth iodide reagent has the drawback that substances other than nicotine are also liable to be precipitated.

[91] J. H. Mueller, *J. Biol. Chem.*, 1916, **25**, 549; *A.*, ii, 541.

[92] A. Madinaveitia and A. González, *Anal. Fis. Quim.*, 1916, **14**, 398; *A.*, ii, 585.

[93] G. D. Beal and St. E. Brady, *J. Ind. Eng. Chem.*, 1916, **8**, 48; *A.*, ii, 356.

[94] H. B. Rasmussen, *Zeitsch. anal. Chem.*, 1916, **55**, 81; *A.*, ii, 359.

[95] G. Bertrand and M. Javillier, *Bull. Soc. chim.*, 1909, [iv], **5**, 241; *A.*, 1909, ii, 450; *Ann. Chim. anal.*, 1911, **16**, 251; *A.*, 1911, ii, 827.

[96] R. Kissling, *Zeitsch. anal. Chem*, 1882, **21**, 64; *A.*, 1882, 1005.

[97] W. Koenig, *Chem. Zeit.*, 1911, **35**, 521, 1047; *A.*, 1911, ii, 670, 1143.

[98] C. C. Keller, *Ber. Deutsch. pharm. Ges.*, 1898, **8**, 145; *A.*, 1899, ii, 193.

[99] J. Tóth, *Chem. Zeit.*, 1911, **35**, 146; *A.*, 1911, ii, 334.

[1] H. Ulex, *ibid.*, 121; *A.*, 1911, ii, 334

[2] H. Thoms, *Ber. Deutsch., pharm. Ges.*, 1900, **10**, 19; *A.*, 1900, ii, 428.

Inorganic Analysis.

Qualitative.—In the ordinary method of separating silver from mercury by treating the mixed chlorides with ammonia, the black precipitate, which consists of a mixture of metallic mercury with the mercuric compound, retains a small amount of the silver in the form of an amalgam. To obviate this, the mercury in the precipitate should be converted into the mercuric state by oxidation with bromine or sodium hypochlorite and nitric acid.[3] An ammoniacal solution of ammonium perchlorate may be used as a sensitive reagent for cadmium, which it precipitates as a white, crystalline, double perchlorate, $[Cd(ClO_4)_2NH_3]$. In applying the test to the mixed sulphides of copper, cadmium, and bismuth, the precipitate is dissolved in nitric acid and an excess of ammonia solution added. The bismuth hydroxide is separated by filtration, and the blue filtrate is treated with the reagent, which precipitates the cadmium even in the presence of five times its quantity of copper.[4]

For the detection of arsenic, the silver nitrate test is very sensitive, a brown coloration being obtained with a solution containing as little as 1 part in 150,000, whilst a distinct precipitate is given by solutions containing 1 part in 60,000. Even when the test is applied in the presence of ammonium nitrate, as formed in ordinary routine analysis, it is still capable of detecting 1 part of arsenic in 15,000.[5]

The dimethylglyoxime test for nickel in the presence of large amounts of cobalt may be rendered much more sensitive by adding alkali cyanide to the solution of the mixed nickel and cobalt salts until the resulting precipitate begins to dissolve, after which the liquid is heated and rotated until its colour changes. It is then diluted with hot water and treated with the reagent, and silver nitrate solution is added drop by drop to precipitate the cyanide as silver argenticyanide and promote the decomposition of the nickelocyanide ions. Under these conditions, the test is capable of detecting 0·02 mg. of nickel, or a tenth of that quantity if the mixture is allowed to remain for twenty-four hours.[6]

A very delicate test for manganese in the presence of large quantities of iron has been based on its oxidation to the manganic condition by means of nitrous acid and the subsequent formation of manganic oxalate, which is of a bright red colour. The test

[3] N. von Zweigbergk, *Zeitsch. anorg. Chem.*, 1916, **93**, 320; *A.*, ii, 344.

[4] R. Salvadori, *Ann. Chim. Applicata*, 1916, **5**, 25; *A.*, ii, 271.

[5] L. J. Curtman and P. Daschavsky, *J. Amer. Chem. Soc.*, 1916, **38**, 1280; *A.*, ii, 491.

[6] A. R. Middleton and H. L. Miller, *ibid.*, 1705; *A.*, ii, 580.

may be conveniently applied by adding an excess of neutral sodium nitrite solution to a neutral solution of the manganous salt and treating the mixture with oxalic acid.[7]

Tungsten in the proportion of 2 per cent. or less in minerals may be detected by the blue coloration which it gives on reduction with metallic tin in hydrochloric acid solution. Columbium gives a similar blue coloration, but may be distinguished by the fact that the colour disappears on dilution, whilst the coloration given by vanadium may also be produced by reduction with tartaric acid, which is not the case with tungsten. Titanium gives a violet coloration under the same conditions.[8] With suitable precautions as to the concentration of the acid, the test is capable of detecting 1 mg. of tungstic acid.[9]

The deposit of selenium, obtained by reducing selenious acid and selenites with zinc and sulphuric acid in Marsh's apparatus, is of a red colour quite distinct from the colour of an arsenic deposit. To distinguish between arsenic and selenium in larger quantities, the hot solution may be treated with hydrogen sulphide. The precipitated sulphur, containing arsenic and selenium sulphides if present, will be brown in the presence of selenium, whilst its colour is not affected by arsenic sulphide. By heating the dry precipitate in a tube, the free sulphur is volatilised, leaving the selenium sulphide as a black mass.

A test for nitrates in the presence of organic matter depends on the fact that an ethereal extract of a solution of salicylic acid in concentrated sulphuric acid gives no red coloration with ferric chloride solution in the absence of nitrates. If nitrosalicylic acid is present, an orange coloration is produced on adding ammonia to the ethereal extract, and a red coloration in the aqueous layer on the addition of dilute ferric chloride solution.[11]

Quantitative.—The advantages of potassium dichromate as a standard for volumetric methods are that the salt can be readily purified and that its solutions are stable, but it has been stated by Wagner and others that it gives too high results on titration. This discrepancy has now been found to be due, in part at least, to the older atomic weights being inaccurate, for comparative estimations have shown that the oxidation follows a course similar to that effected by potassium permanganate. The slightly high results (0·13 per cent.) are attributable, not to any property inherent in the dichromate, such as its promoting catalytic oxidation, but to

[7] W. Prandtl, *Ber.*, 1916, **49**, 1613; *A.*, ii, 621.
[8] M. L. Hartman, *Chem. News*, 1916, **114**, 27; *A.*, ii, 494.
[9] M. L. Hartman, *ibid.*, 45; *A.*, ii, 495.
[10] J. Meunier, *Compt. rend.*, 1916, **165**, 332; *A.*, ii, 641.
[11] A. Tingle, *J. Soc. Chem. Ind.*, 1916, **35**, 77; *A.*, ii, 195.

differences in the methods of titration. The best method of standardisation is gravimetric estimation with oxalic acid. It is not possible to use dichromate as a standard acid in alkalimetry, since the acidity of the solution increases with the concentration.[12]

A convenient method of estimating certain bivalent metals is to titrate their phosphates with standard acid.[13] In the case of magnesium, it is advisable to use 50 per cent. alcohol in place of the ammoniacal solution for washing the precipitated magnesium ammonium phosphate. Zinc ammonium phosphate and cadmium ammonium phosphate may also be directly titrated in the same way, cochineal being used as indicator, but the method gives unsatisfactory results with manganese. The precipitated cobalt ammonium phosphate varies in properties with the mode of preparation. The precipitate obtained by Clarke's method[14] is suitable for direct titration with acid, but a double precipitation is advisable to remove traces of nickel. The nickel in the filtrate may be accurately estimated by titration with cyanide solution.

It is possible to utilise the reducing action of titanium chloride in several ways in volumetric analysis. Thus, ferric chloride and chromates may be accurately titrated in hot hydrochloric acid solution with methylene-blue as indicator, whilst cupric salts may be estimated in the same way with safranine or induline as indicator. For the estimation of titanium in ores, the sample is fused with alkali, dissolved in hydrochloric acid, and the solution reduced with zinc and treated with standard ferric chloride solution, the excess of which is titrated with titanium trichloride in an atmosphere of carbon dioxide.[15]

From the results of a study of the oxidations effected by potassium permanganate in alkaline solution, it appears that the products may vary with the degree of alkalinity. For example, in a slightly alkaline solution, nickel is oxidised to an oxide, $Ni_{10}O_{11}$, whilst in strongly alkaline solution an oxide approximating in composition to Ni_2O_3 is produced. Oxidation of cobalt in strongly alkaline solution yields an oxide containing slightly more oxygen than is required by the formula Co_2O_3. In the titration of arsenious acid in strongly alkaline solution, the permanganate is reduced to the manganic condition when potassium sulphate or other electrolyte is present to cause precipitation of colloidal

[12] G. Bruhns, *J. pr. Chem.*, 1916, [ii], **93**, 73, 312; *A.*, ii, 337, 581.
[13] W. R. Schoeller and A. R. Powell, *Analyst*, 1916, **41**, 124; *A.*, ii, 346.
[14] *Chem. News*, 1883, **48**, 262.
[15] A. Monnier, *Ann. Chim. anal.*, 1916, **21**, 109; *A.*, ii, 444.

manganese hydroxide. Should the colloidal hydroxide remain in suspension, however, the reduction of the manganese continues to the manganous condition. Thallous and cerous salts are quantitatively oxidised to thallic and ceric salts, and selenious and tellurous acids to selenic and telluric acids respectively. In the case of lead, however, the oxidation is incomplete.[16]

Several useful applications of iodometric methods have been brought forward during the year. A differential method of estimating periodates, iodates, bromates, and chlorates has been based on the different conditions under which they react with iodine solutions. For example, periodates are quantitatively decomposed into iodates and free iodine when treated with a solution of iodine in a saturated solution of boric acid containing borax to reduce the acidity. Both iodates and periodates react with a solution of iodine in $N/4$-acetic acid, and the liberated iodine may be titrated. A dilute ($N/2$) hydrochloric acid solution of iodine reacts with bromates, whilst a solution of $6N$-strength reacts with chlorates, leaving perchlorates unaffected.[17] The presence of hypochlorites does not affect the accuracy of the results obtained in the estimation of chloric acid and chlorates by this method.[18]

It has long been recognised that thiosulphates and sulphites are formed when tetrathionate solutions are treated with hot concentrated alkali hydroxides, and it has now been shown that the reaction also takes place fairly rapidly in cold and dilute solutions.[19] Hence, in titrating solutions containing tetrathionate, it is essential not to render the liquid alkaline. Should this be temporarily unavoidable, as, for instance, in the case of a solution to which iodine and excess of thiosulphate have been added, it is best to use the smallest possible amount of sodium carbonate and to keep the temperature low. It is also advisable to saturate the liquid with carbon dioxide.

In the iodometric estimation of gold by Peterson's method,[20] the results are rendered more accurate by treating the compound, $AuCl_3$,HCl, with potassium iodide and iodate and titrating the liberated iodine. The gold salt is first converted into gold chloride and free hydrochloric acid, and the latter reacts with the iodate, forming free iodine and potassium chloride. Hence, in analysing gold chloride, $AuCl_3$,H_2O, by this method, the difference in the results obtained on titrating the iodine liberated from potassium

[16] B. Brauner, *Zeitsch. anal. Chem.*, 1916, **55**, 225; *A.*, ii, 437.
[17] O. L. Barnebey, *J. Amer. Chem. Soc.*, 1916, **38**, 330; *A.*, ii, 261.
[18] R. L. Taylor, *J. Soc. Dyers*, 1916, **32**, 68; *A.*, ii, 193.
[19] R. M. Chaplin, *J. Amer. Chem. Soc.*, 1916, **38**, 625; *A.*, ii, 261.
[20] H. Peterson, *Zeitsch. anorg. Chem.*, 1898, **19**, 59; *A.*, 1899, ii, 250.

iodide and from a mixture of potassium iodide and iodate affords a measure of free hydrochloric acid if present.[21]

In the absence of reducing compounds, such as ferrous, cuprous, and antimonous salts, or of precipitated metals, tin in the stannous condition may be titrated with potassium iodate solution. The reagent is run into the strongly acid solution of the stannous salt, to which has been added a little chloroform, and the stoppered bottle is shaken after each addition until the chloroform, which has absorbed liberated iodine, is decolorised. Stannic solutions are conveniently reduced with metallic nickel. With suitable modifications, the method is applicable to the analysis of solders, bronzes, etc.[22]

A rapid method of estimating mercury is based on the reduction of mercuric salts by means of formaldehyde in the presence of sodium hydroxide or potassium hydroxide. The reduced metal is then quantitatively converted into mercuric iodide by treatment with standard iodine solution, the excess of which is titrated in the usual way.[23]

Cobalt salts may be readily oxidised by means of hydrogen peroxide or sodium perborate, preferably the latter, and on this reaction has been based a method of estimating cobalt. After removal of the excess of the oxidising agent, the solution is acidified and treated with an excess of potassium iodide, and the liberated iodine is titrated with thiosulphate solution which has been standardised on a solution of a pure cobalt salt. The method is applicable in the presence of nickel and alkalis, but the solution must not contain iron, manganese, or any substances capable of liberating iodine from potassium iodide.[24]

A volumetric method of estimating thiosulphates in the presence of sulphites depends on the fact that mercuric chloride reacts with sulphites to form soluble double salts, whilst it decomposes thiosulphates, with the liberation of free sulphuric acid, the titration of which affords a measure of the thiosulphate. The precipitation of mercuric oxide by the alkali during the titration is prevented by the addition of ammonium chloride.[25]

A new method of estimating fluorine is based on its precipitation as thorium fluoride from an acid solution and ignition of the precipitate, which leaves a residue of thorium oxide. The chief

[21] L. Vanino and F. Hartwagner, *Zeitsch. anal. Chem.*, 1916, **55**, 377; *A.*, ii, 582.

[22] G. S. Jamieson, *J. Ind. Eng. Chem.*, 1916, **8**, 500; *A.*, ii, 451.

[23] G. Adanti, *Boll. chim. farm.*, 1916, **55**, 553; *A.*, ii, 579.

[24] W. D. Engle and R. G. Gustavson, *J. Ind. Eng. Chem.*, 1916, **8**, 901; *A.*, ii, 649.

[25] A. Sander, *Zeitsch. anal. Chem.*, 1916, **55**, 340; *A.*, ii, 536.

precaution necessary is not to add too large an excess of thorium nitrate, which tends to redissolve the precipitate. Silicofluorides may be precipitated directly in the same way, whilst tantalofluorides should be boiled with sodium carbonate and filtered from the tantalic acid before precipitation of the fluorine.[26]

The low results sometimes obtained in the estimation of silica in silicates are partly due to the fact that silica is somewhat soluble in solutions of sodium chloride. To obviate this, it is necessary to use as small a proportion as possible of sodium carbonate for the fusion of the silicate. Silica is also sparingly soluble in hydrochloric acid, and hence one evaporation does not effect a complete separation. Acid of specific gravity 1·1 has less solvent action on silica than stronger or weaker acid. The first evaporation should be carried out as rapidly as possible, whilst the final dehydration should not occupy more than two hours at a temperature not exceeding 110°.[27]

In the estimation of nitrogen by Kjeldahl's method, the use of mercury to accelerate the conversion causes the results to be too low in the case of certain compounds, such as caffeine, uric acid, and pure ammonium sulphate. By using copper foil in place of mercury, the correct results are obtained with ammonium sulphate, and the loss of nitrogen in the case of the other compounds is greatly reduced.[28]

The method of distilling the ammonia by the introduction of a current of cold purified air[29] gives good results in the case of many compounds, but in other cases the yield of nitrogen is from 0·3 to 1·97 per cent. lower than that obtained by the ordinary method of distillation. For the analysis of substances of unknown composition, the method must therefore be regarded as untrustworthy.[30]

The use of magnesia, which is suggested as the most suitable alkali for the decomposition of the ammonium sulphate in this process,[31] is open to the objection that part of the ammonia may be retained in the distillation flask as ammonium magnesium phosphate.

As commonly used, the method of estimating arsenic by reduction with ferrous salts and distillation as trichloride, frequently gives low results. To render the method trustworthy, it is essential

[26] F. Pisani, *Compt. rend.*, 1916, **162**, 791 ; *A.*, ii, 393.

[27] V. Lenher and E. Truog, *J. Amer. Chem. Soc.*, 1916, **38**, 1050 ; *A.*, ii, 396.

[28] O. Nolte, *Zeitsch. anal. Chem.*, 1916, **55**, 185 ; *A.*, ii, 341.

[29] P. A. Kober, *J. Amer. Chem. Soc.*, 1908, **30**, 1131 ; *A.*, 1908, ii, 776.

[30] K. G. Falk and K. Sugiura, *ibid.*, 1916, **38**, 916 ; *A.*, ii, 341.

[31] R. S. Davisson, E. R. Allen, and B. M. Stubblefield, *ibid.*, 896 ; *A.*, ii, 643.

that only a small proportion of arsenic should be present, and cuprous chloride should be used in place of ferrous chloride as the reducing agent. The arsenic trichloride may then be distilled in a current of hydrogen chloride, and the distillate rendered alkaline, and, after the addition of sodium hydrogen carbonate in excess, titrated with standard iodine solution.[32]

A new method of estimating cadmium depends on its precipitation as dipyridine cadmium chloride, $CdCl_2,2C_5H_5N$, which is converted into the monopyridine compound when heated at 115° to 120°. The latter is stable, and can be dried at temperatures up to 140° without decomposition. The corresponding cupric pyridine compound is fairly readily soluble in pyridine solutions, and this difference from the cadmium compound may be utilised in the qualitative separation of the two metals, although the quantitative results thus obtained are only approximately correct.[33]

A modification of Volhard's method is especially suited for the estimation of copper and iron in ores, since it enables both metals to be estimated in the same solution. The copper is precipitated as cuprous thiocyanate and the iron is titrated with potassium permanganate solution. In preparing the ores, the sample is decomposed with nitric and hydrochloric acids in the usual way, these acids being subsequently expelled by heating the liquid with sulphuric acid, after separation of any silver chloride.[34]

It has been accepted that in estimating carbon in steel, higher results are obtained by increasing the temperature of the combustion in oxygen, although the conclusion does not appear to have been based on trustworthy experiments. A recent investigation in which the temperature was maintained at 1500° has shown that the amounts of carbon thus obtained agreed within 0·015 per cent. with those given by more simple methods of direct combustion.[35]

Baudisch's "cupferron" reagent (ammonium salt of nitrosophenylhydroxylamine) has been found applicable to the separation of metals other than those previously described. Thorium is quantitatively precipitated by it from an acetic acid solution, but the results are not claimed to be as trustworthy as those given by the oxalic acid method.[36] Thorium differs in this respect from zirconium, which requires the presence of sulphuric acid for its quantitative precipitation by the reagent.[37]

[32] R. C. Roark and C. C. MacDonnell, *J. Ind. Eng. Chem.*, 1916, **8**, 327; *A.*, ii, 342. [33] S. Kragen, *Monatsh.*, 1916, **37**, 391; *A.*, ii, 647.

[34] G. Edgar, *J. Amer. Chem. Soc.*, 1916, **38**, 884; *A.*, ii, 346.

[35] J. R. Cain and H. E. Cleaves, *J. Ind. Eng. Chem.*, 1916, **8**, 321; *A.*, ii, 343. [36] W. M. Thornton, jun., *Chem. News*, 1916, **114**, 13; *A.*, ii, 495.

[37] W. M. Thornton, jun., and E. M. Hayden, jun., *Amer. J. Sci.*, 1914, [iv], **38**, 137; *A.*, 1914, ii, 779.

"Cupferron" also precipitates vanadium quantitatively from acid solutions of ammonium metavanadate, and on igniting the precipitate a residue of the oxide, V_2O_5, is left. It is essential that the solution should not contain more than 1 per cent. of hydrochloric or sulphuric acid.[38]

With suitable modifications the method is also applicable to the separation of vanadium from phosphoric and arsenic acids, and from uranium, but in presence of the latter the results for vanadium are a little high. The uranium may be precipitated from the filtrate by ammonia (after addition of ammonium chloride), and the results thus obtained are accurate.[39]

Fieber's method of estimating tungsten has been tested and found to yield accurate results in the analysis of ferro-tungsten. With slight modifications it is also suitable for tungsten concentrates containing up to 10 per cent. of tin. Any traces of tin left in the final precipitate of tungstic acid are expelled by volatilisation with ammonium chloride.[41]

Potassium in the presence of large amounts of sodium may be most accurately estimated by precipitating it with cobalt nitrite,[42] dissolving the precipitate in hydrochloric acid, and making the final estimation by the perchlorate method, thus eliminating substances which interfere with the accuracy of the latter.[43] The combined method is not applicable in the presence of ammonium salts, whilst phosphates of iron or aluminium, if present, should be kept in solution by the addition of sodium citrate prior to the precipitation of the potassium with cobalt nitrite.[44]

Electrochemical Analysis.

A useful method for titrating vanadates with ferrous sulphate solution has been devised, in which the change in the electromotive force of a galvanic battery is used to indicate the end-point of the reaction. The apparatus comprises a resistance box of two coils and sliding contacts arranged so as to vary the *E.M.F.* of the dry cells. The solution of the vanadate is treated with dilute sulphuric acid, and the ferrous sulphate solution run in until the galvanometer needle, which becomes practically steady towards the end of the titration, makes a sudden move, indicating the addition of an

[38] W. A. Turner, *Amer. J. Sci.*, 1916, [iv], **41**, 339; *A.*, ii, 347.
[39] W. A. Turner, *ibid.*, 1916, [iv], **42**, 109; *A.*, ii, 540.
[40] R. Fieber, *Chem. Zeit.*, 1912, **36**, 334; *A.*, 1912, ii, 495.
[41] E. Dittler and A. von Graffenried, *ibid.*, 1916, **40**, 681; *A.*, ii, 582.
[42] E. Mitscherlich and H. Fischer, *Landw. Versuchs-Stat.*, 1912, **78**, 74; *A.*, 1912, ii, 996.
[43] R. G. Thin and A. C. Cumming, *T.*, 1915, **107**, 361; *A.*, 1915, ii, 281.
[44] A. H. Bennett, *Analyst*, 1916, **41**, 165; *A.*, ii, 448.

excess of the reagent. The correct figure is then found by titrating the liquid with standard dichromate solution until the needle returns to the place where it was before its sudden move. The method gives results in close agreement with those obtained by the usual standard methods.[45]

By the use of suitable modifications the method is also applicable to the estimation of chromium and vanadium in steel.[46]

It has already been shown [47] that copper and tin may be precipitated by an electric current from their solution in nitro-hydrofluoric acid, leaving lead and antimony in solution, and later experiments have shown that the same method may be used for separating silver and mercury from tin, antimony, tungsten, and molybdenum. The silver deposits usually contain no appreciable quantity of platinum, but the mercury deposited on the anode usually contains a considerable proportion of platinum, the amount depending on such factors as the quantities of tin and hydrofluoric acid, and the duration of the electrolysis. The necessary correction may be obtained by treating the deposit with nitric acid and estimating the undissolved platinum.[48]

It is commonly accepted that it is not practicable to obtain good deposits of metals from solutions of their chlorides owing to the subsequent oxidation caused by the liberated chlorine, but recent work has shown that under suitable conditions this action may be prevented.[49] To obtain satisfactory electrolytic deposits of antimony, bismuth, copper, lead, tin, and cadmium from solutions of the metals in hydrochloric acid, it is necessary to add a suitable reducing agent, such as hydroxylamine hydrochloride, and to see that no nitric acid or oxides of nitrogen are present.

Silver may also be estimated in the same way by electrolysing solutions of silver chloride in ammonia. The deposits are purer than those obtained in the electrolysis of cyanide solutions, and the method gives trustworthy results.[50]

An electrolytic method of estimating zinc gives good results, provided that certain conditions are maintained, such as the degree of acidity of the electrolyte and the uniform density of the current on the cathode.[51] The zinc is converted into sulphate, and is deposited from dilute sulphuric acid solution to which has been added

[45] G. L. Kelley and J. B. Conant, *J. Amer. Chem. Soc.*, 1916, **38**, 341 ; *A.*, ii, 274.

[46] G. L. Kelley and J. B. Conant, *ibid.*, 719 ; *A.*, ii, 540.

[47] L .W. McCay, *ibid.*, 1914, **36**, 2375 ; *A.*, 1914, ii, 856.

[48] L. W. McCay and N. H. Furman, *ibid.*, 1916, **38**, 640 ; *A.*, ii, 273.

[49] E. P. Schoch, D. J. Brown, and T. E. Phipps, *ibid.*, 1660 ; *A.*, ii, 578.

[50] E. P. Schoch and F. M. Crawford, *ibid.*, 1682 ; *A.*, ii, 576.

[51] F. Chancel, *Bull. Soc. chim.*, 1916, **19**, 59 ; *A.*, ii, 198.

a quantity of sodium formate corresponding with the amount of metal. The cathode consists of sheet platinum and the anode of platinum wire.[52] The method is also applicable to brass after removal of iron by precipitation.

Water Analysis.

For the estimation of dissolved oxygen in water, Winkler's modified method[53] has stood the test of critical examination from several quarters, and may now be accepted as generally trustworthy. The modifications suggested during the past year have not claimed to yield more accurate results, but have had for their object the simplification of working details. Such modifications, for example, are the use of potassium iodide in solid form, and the titration of the liquid in the original bottles.[54] The presence of nitrites or organic matter in the water interferes with the estimation. One method of eliminating this influence is to treat the water with dilute sulphuric acid and a slight excess of calcium hypochlorite solution prior to the estimation of the oxygen by the manganous chloride method. At the same time a blank test is made to ascertain the effect of the excess of chlorine on the results of the titration, by treating an equal volume of the water with the same quantities of sulphuric acid and calcium hypochlorite, adding a trace of potassium iodide, and titrating the liberated iodine.[55]

Another means of inhibiting the effect of nitrites and organic matter is to convert the manganous hydroxide into carbonate by the addition of solid potassium hydrogen carbonate, to collect the precipitate, and to treat it with potassium iodide and acid.[56] If ferrous salts are present, they should be oxidised by means of permanganate, and the water should then be acidified with phosphoric acid instead of with hydrochloric acid.[56] None of the suggested modifications is trustworthy when organic matter is present in large quantities, as in certain trade effluents, and in such cases a gas-volumetric method of estimating the dissolved oxygen must be used.[57]

A simple method of detecting methane in the gases separated from water consists in first absorbing the oxygen in the usual manner, and then treating the residue with *iso*butyl alcohol which has previously been saturated with air. Methane, if present, will

[52] See F. Chancel, *Bull. Soc. chim.*, 1913, [iv], **13**, 74; *A.*, 1913, ii, 236.

[53] L. W. Winkler, *Zeitsch. anal. Chem.*, 1914, **53**, 665; *A.*, 1915, ii, 277.

[54] G. Bruhns, *Chem. Zeit.*, 1915, **39**, 845; *A.*, 1916, ii, 47; *Chem. Zeit.*, 1916, **40**, 45, 71; *A.*, ii, 146.

[55] L. W. Winkler, *Zeitsch. angew. Chem.*, 1916, **29**, i, 44; *A.*, ii, 194.

[56] G. Bruhns, *Chem. Zeit.*, 1916, **40**, 45, 71; *A.*, ii, 146.

[57] L. W. Winkler, *Zeitsch. Nahr. Genussm.*, 1915, **29**, 121; *A.*, ii, 487.

be absorbed by the reagent, and there will be a decrease in the volume of the gas, whereas the volume of nitrogen will not be affected.[58]

Rapid methods of sterilising water are of paramount importance at the present time, especially such as are applicable for the use of armies in the field. In one of these methods a reagent containing active chlorine is prepared by treating a solution of sodium hypochlorite with potassium permanganate, and the excess of chlorine in the water is subsequently destroyed by means of thiosulphate.[59] Any traces of thiosulphate left in the water may be detected and colorimetrically estimated by means of silver nitrate, followed by just sufficient ammonia to dissolve all silver chloride.[60] A sensitive reagent for free chlorine in water which has been treated with alkaline hypochlorite is an acid solution of hexamethyltri-*p*-aminotriphenylmethane, which gives an immediate violet coloration with water containing as little as 3 parts of free chlorine in 100,000,000. An advantage which this reagent has over the potassium iodide–starch reagent for free chlorine is that it is not readily affected by nitrites.[61]

Of late years there has been a tendency to attach undue weight to the results of oxygen absorption tests in the analysis of water, and in some cases when the conclusions to be drawn from the general results have been doubtful the permanganate test has been made the decisive factor. Although there can be no question as to the value of the test for following any variations in the purity of a water supply, the uncertainty in the results due to such factors as the temperature, duration of action, and the amount of excess of permanganate renders the method untrustworthy for a water of unknown origin.[62]

In any case, oxidation in alkaline solution must be regarded as liable to grave error from the fact that there is a tendency for the permanganate to be reduced to manganate through the catalytic action of the bulky precipitate of manganese dioxide.[63] Hence, the results obtained with an acid permanganate solution are more trustworthy, notwithstanding the fact that the effect of chlorine in the water is minimised by the use of an alkaline solution. Under any conditions, however, it is preferable to remove the chlorine by means of silver oxide before estimating the oxygen absorption. The influ-

[58] L. W. Winkler, *Zeitsch. angew. Chem.*, 1916, **29**, i, 218; *A.*, ii, 448.
[59] H. Penau, *J. Pharm. Chim.*, 1916, [vii], **13**, 377.
[60] J. Golse, *ibid.*, 1916, **14**, 8.
[61] G. A. Le Roy, *Compt. rend.*, 1916, **163**, 226; *A.*, ii, 535.
[62] G. W. Heise and R. H. Aguilar, *Philippine J. Sci.*, 1916, [A], **11**, 37; *A.*, ii, 576.
[63] J. H. Sachs, *J. Ind. Eng. Chem.*, 1916, **8**, 404; *A.*, ii, 399.

ence of the quantity of the reagent is most pronounced at higher temperatures. At 85° the absorption of oxygen increases with the amount of permanganate added, whereas at 37° variations in the quantities added have but little effect on the results. This temperature is therefore the best for accelerating the absorption whilst eliminating to a considerable extent the quantity factor.[64]

Recently proposed methods of estimating the hardness of water must be regarded as, in the main, either modifications of Hehner's method[65] or of Clark's soap test, in which an alkali salt of a pure fatty acid takes the place of the soap solution. In Wartha's method of estimating the alkalinity by titrating the boiling water with standard hydrochloric acid, the use of alizarin as indicator gives sharper results than when methyl-orange is used, although with the latter indicator there is no need to boil the water.[66] Iron salts, if present, must be eliminated prior to the titration.

A convenient modification for estimating the total hardness is to evaporate the water with standard potassium carbonate solution, to extract the residue with 90 per cent. alcohol, and to titrate the filtered extract with standard hydrochloric acid, with methyl-orange as indicator. This method is based on the facts that calcium and magnesium carbonates are practically insoluble in alcohol of that strength, whilst the double carbonate of magnesium and potassium which may be formed is decomposed, with precipitation of the magnesium carbonate and solution of the potassium carbonate, which, unlike sodium carbonate, is fairly readily soluble in strong alcohol.[67]

Blacher's method,[68] in which pure potassium palmitate is used for titrating the total hardness, has proved more generally applicable than methods involving the use of salts of other fatty acids. It has the drawback that after the temporary hardness has been estimated by titration with standard hydrochloric acid, it is not easy to ascertain whether all the free carbon dioxide has been expelled. This is easily obviated by neutralising the free carbon dioxide with $N/10$-potassium hydroxide solution, with phenolphthalein as indicator, prior to the titration with potassium palmitate solution.[69]

As a rapid means of checking the chemical estimation of the hardness, the electrical conductivity of the water may be deter-

[64] J. H. Sachs, *loc. cit.* [65] O. Hehner, *Analyst*, 1883, **8**, 77.

[66] L. W. Winkler, *Zeitsch. angew. Chem.*, 1916, **29**, i, 218; *A.*, ii, 448.

[67] S. A. Kay and S. H. Newlands, *J. Soc. Chem. Ind.*, 1916, **35**, 445; *A.*, ii, 344.

[68] C. Blacher, P. Grünberg, and M. Kissa, *Chem. Zeit.*, 1913, **37**, 56; *A.*, 1913, ii, 153.

[69] M. Tilgner, *ibid.*, 1916, **40**, 675; *A.*, ii, 577.

mined by means of an apparatus such as the "dionic water tester."[70] There should be an approximate relationship between the two results, each 20 units of electrical conductivity corresponding with one degree of hardness.[71]

For the separate estimation of calcium and magnesium, advantage may be taken of the fact that whereas magnesium carbonate is soluble in an excess of ammonium carbonate solution, calcium carbonate is almost insoluble therein, and may be estimated in the insoluble residue by titration with standard acid. The difference between the result and the total hardness determined by the alcohol method (see above) will give the amount of magnesium.[72]

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[70] L. Archbutt, *Analyst*, 1912, **37**, 538.

[71] S. A. Kay and S. H. Newlands, *J. Soc. Chem. Ind.*, 1916, **35**, 445; *A.*, ii, 344.

[72] S. A. Kay and S. H. Newlands, *ibid.*, 447; *A.*, ii, 345.

PHYSIOLOGICAL CHEMISTRY.

Arrhenius, as is well known, has applied the accurate methods of physical chemistry to the complex phenomena of immunity, and, in a book recently published in English,[1] he has brought together many of the quantitative data which exist in the literature concerning the reactions of the animal body to antigens. He has treated them, as well as the subject of enzymic action in general, from the mathematical point of view of the physical chemist. It is remarkable to realise how much of the available material proves itself amenable to such treatment. The writings of so great a teacher as Arrhenius cannot but have a very healthy influence on biochemistry. I venture to think, however, that he takes too one-sided a view with regard to the methods likely to lead to progress in the immediate future.

In the preface to his book he writes: "The aversion shown by biochemists, who have in most cases a medical education, to exact methods is very easily understood. They are not acquainted with such elementary notions as 'experimental errors,' 'probable errors,' and so forth, which are necessary for drawing valid conclusions from experiments."

Under that criticism many biochemists of to-day, although by no means all, must—with certain self-defensive reservations—bow their heads. When, however, a science is largely in its descriptive stage, it would be a pity if any of its devotees allowed themselves to be too much discouraged by particular deficiencies in their education, especially when that education happens to be one which, at any rate, makes them, better than anyone else, able to appreciate the nature of the problems to be solved. We all know that to arrive at the mathematical form is the ultimate goal of all real scientific knowledge; but at a given moment in the history of a science, the acquirement of new qualitative knowledge may be as important as the consolidation of other knowledge in a mathematical form. In biochemistry, which is just now busy in

[1] "Quantitative Laws in Biological Chemistry." London: G. Bell & Sons, 1915.

collecting its data, the mere discovery of hitherto unknown reactions in the animal body, with a supply of information concerning their locality and their significance to the body as a whole, may well lead to more profitable suggestions for work in the immediate future than the proof that this or that reaction is strictly unimolecular, or that the laws of equilibria apply with exactness in such cases as the binding of toxins by antitoxins. It is, I think, only honest to admit that whilst the quantitative must in some sort enter into every investigation, to demand it in a particular form at a given moment may savour of the doctrinaire. Moreover, the methods of physical chemistry, when applied to phenomena in which what we call "physical" does not completely outweigh what we still call "chemical," may, in arriving by a short cut at accuracy of statement, leave us ignorant of just those details which are most necessary for the guidance of further research. To biology in its present position the chemical details are of great importance.

We know, it is true, almost nothing about the pure chemistry of the materials and agents which play their part in the phenomena of immunity, or in such events as the coagulation of the blood. For this reason, it is perhaps scarcely fair to appraise the research done on them under headings avowedly chemical; but the chemical knowledge is urgently desired, and it will come the sooner if the attention of chemists be directed to the problems.

The Coagulation of the Blood.

This subject received treatment from Professor Halliburton in the Report for 1912,[2] but in order to make clear the significance of the progress recently made, it seems necessary to give a very brief résumé of the present position, even although it involves some repetition of what has already appeared in these Reports.

Any divergence in the views at present held with regard to the essential nature of the process (as distinct from its details) arises from a difference in the degree of importance ascribed to catalytic factors. The older view, based upon the researches of Buchanan and Alexander Schmidt, was developed by Hammarsten, and expanded a few years ago by Morawitz, Fuld, J. Mellanby, and others. It ascribes the initiation of coagulation to the appearance in shed blood of catalytic agents which are either absent from the circulating fluid (being held in the formed elements and the tissues) or are there balanced by anti-coagulative agents. This view involves the belief that chemical change precedes clot formation.

[2] See *Ann. Report*, 1912, 236.

From the other point of view, blood coagulation is considered as due to a rearrangement in an unstable system of associated colloids, initiated perhaps by the addition of fresh colloids from the formed elements of the blood or from tissue cells. This rearrangement may involve some change in pre-existing loose associations between colloid and colloid, but not necessarily a chemical change in any strict sense. The process is thus essentially physicochemical in nature. Although the fact is not always recognised, chiefly because there is so great a breach between the terminology of to-day and that of thirty years ago, this view owes its parentage to Woolridge. It was much later supported in the somewhat involved publications of Nef, and has received recent support from America, especially in papers from the laboratory of W. H. Howell. I note that A. P. Mathews gives strong support to the conception of blood coagulation as a purely physicochemical process in his excellent "Text-book of Physiological Chemistry,"[3] which, although it was published last year, received no reference in my last Report.

So brief a statement as the above may make the cleavage of opinion seem sharper than it really is, but I think it fairly represents two existing currents of thought about the matter.

It is still generally agreed that the following factors are concerned in the phenomenon: first, the fibrinogen of the plasma, the essential material precursor of the clot; secondly, an agent, thrombin, which is essential for the conversion of fibrinogen into fibrin. This has long been looked upon as an enzyme, but Howell holds that it should be removed from that category because, according to his observations, increasing amounts of thrombin give increasing amounts of fibrin, and the weight of fibrin produced by a given submaximal amount of thrombin is not affected by the time during which the thrombin is allowed to act. In any case, thrombin is not present as such in the blood, but in the form of a precursor, prothrombin. For the conversion of prothrombin into thrombin there is needed yet another factor, thrombokinase or thromboplastin. This exerts its influence only in the presence of calcium salts. It is not present in the circulating blood, but is supplied at the moment of shedding either from the leucocytes or from the extraneous tissues. In the theory of Morawitz it is a dynamic "activator" of prothrombin. On this view, the kinase presumably acts as catalyst to some chemical change. Its entry into the plasma gives the initial impulse to the changes which finally result in clot formation.

The maintenance of fluidity in circulating blood is due, how-

[3] New York, William Wood and Company, 1915.

ever, not alone to the absence of kinase, but also to influences which inhibit the action of thrombin. These inhibitory effects are collectively attributed to "antithrombin." Howell treats of "antithrombin" as a quite definite substance, and his theory of coagulation gives much prominence to it. According to him, the conversion of prothrombin into thrombin calls for the action of calcium, and for that alone. This action does not occur in circulating blood or in a stable plasma, because in them the prothrombin is combined with antithrombin. Thrombokinase (thromboplastin in Howell's nomenclature) is not an "activator" in the previously accepted sense. It exerts its influence by combining with antithrombin, so liberating prothrombin from its combination with that substance and leaving it open to the influence of calcium. This view is apparently supported by Howell's observation that if plasma is treated with acetone and the resulting precipitate washed with ether, an aqueous solution of the precipitate yields active thrombin on the addition of calcium alone. According to Howell,[4] it contains no kinase, because it will not clot peptone plasma. It contains prothrombin which is open to the influence of lime salts, because it has been freed from antithrombin. H. H. Dale and G. S. Walpole,[5] however, in a paper with which I am about to deal, state that they have hitherto failed to obtain on Howell's lines a preparation with such properties, and they point out that, in any case, the proof of the absence of kinase is unsatisfactory. These authors generally criticise the experiments upon which Howell bases his views, and supply what seems to be very conclusive evidence to show that there is no real antagonism between the actions of kinase and antithrombin, and therefore that Howell's view as to the function of the former is unjustified.

The paper of Dale and Walpole is one which marks real progress in the subject. It describes improvements in technique which yield a series of preparations such that each exhibits—uncomplicated by any other action—the activities of some one of the factors demanded by the theory of Morawitz. The mutual influence and relations of the various factors is thus made particularly clear, and the views of Morawitz are confirmed.

The interest of the paper is, however, by no means confined to points of criticism or technique. It deals with the mode of origin of thrombokinase, and in this connexion supplies facts of quite unusual interest.

[4] *Amer. J. Physiol.*, 1914, **35**, 474 ; *A.*, 1915, i, 35.
[5] *Biochem. J.*, 1916, **10**, 331 ; *A.*, i, 859.

Recent work by others[6] has shown that when serum is shaken with chloroform it acquires remarkable toxic properties. This observation, as a matter of fact, led to the present work of Dale and Walpole, whose concern was primarily with the study of anaphylaxis. G. R. Minot[7] has shown that such treatment with chloroform destroys antithrombin. Dale and Walpole confirm this, and find that the destruction is both rapid and complete. When stable fowl's plasma is shaken with twice its volume of chloroform it clots, and the resulting serum is found to be rich in free thrombin. Now, as the plasma loses its antithrombin under this treatment, the result is, at first sight, in favour of Howell's theory. The chloroform, in effect, seems to act as kinase is, by him, assumed to act, liberating thrombin by the removal of its inhibitor. It is found, however, that a minute proportion of the chloroform-treated plasma when mixed with fresh stable plasma will cause this to clot with great rapidity, although it contains all its original supply of antithrombin. Moreover, chloroform does not yield free thrombin from such preparations of prothrombin as (on Howell's view) would contain it in combination with antithrombin, although kinase activates these preparations at once. Further experiments showed that, as a matter of fact, chloroform initiates coagulation in a stable plasma, not because it destroys antithrombin, but because it induces the liberation of kinase, from which the plasma was previously free. This is certainly an interesting result, and its explanation is still more interesting.

Chloroform destroys not only the antithrombin, but also the antitryptic factor or factors in serum, as Jobling and his co-workers[8] have shown; trypsin is thus unmasked, and proteolytic activity appears in the fluid. Now this fact suggests a possible clue to the appearance of the thrombokinase in plasma. Dale and Walpole added trypsin under carefully controlled conditions to stable bird's plasma, and demonstrated completely that as soon as it is in excess of the antitrypsin, kinase is liberated. Chloroform thus causes plasma to coagulate, because by destroying antitrypsin it initiates proteolysis, which is followed by the liberation of kinase. "It may be," the authors write, "that some degree of protein cleavage is the necessary preliminary to the liberation of kinase from any tissue: and that the ease with which it appears on cell injury and the relatively drastic treatment needed for its production in a stable avian plasma represent a differing delicacy in the poise in the balance between proteolytic ferment and those

[6] Jobling and Peterson. *J. Exp. Med.*, 1914, **19**, 481, with other papers in succeeding volumes.

[7] *Amer. J. Physiol.*, 1915, **39**, 131; *A.*, i, 100.

[8] *loc. cit.*

antagonistic influences which, in the case of the plasma, we summarily describe as 'antitrypsin.'"

Thrombokinase is certainly, from the biological point of view, a most interesting and important agent. Howell believes that it is identical with the phosphatide kephalin, and, under his direction, J. McLean[9] has recently sought for further evidence in support of this view. He prepared kephalin from various sources, and, having purified his products as completely as possible, found that they all displayed the properties of kinase. This evidence gains in significance from the fact that other phosphatides were found by McLean to be quite inactive. C. A. Pekelharing[10] has also shown that ordinary lecithins are without kinasic action. Recent work by P. A. Levene and C. J. West[11] seems to show that kephalin as obtained from quite diverse tissues is one and the same substance, and, as its actual constitution is within measurable distance of being accurately known, it would seem that in the identification of kinase with kephalin a real step forward has been made in the basal chemistry of blood coagulation. When we remember, however, how stable may be the association between certain enzymes and lipoids, we may still feel that a final proof of the identity will not come until kephalin has been synthesised and the kinasic powers of the artificial product demonstrated.

J. C. Wakelin Barrett[12] has made a quantitative study of the relations which obtain between the time of coagulation of fibrinogen and the amount of thrombokinase concerned in the process. He claims to have established the significant fact that a given quantity of kinase in the presence of calcium chloride and a sufficient amount of prothrombin will produce a definite quantity of thrombin which is independent of the actual concentration of prothrombin. He states, moreover, although I do not fully appreciate the evidence for the statement, that when a mixture of prothrombin, fibrinogen, and calcium salts coagulates under the influence of added kinase, the coagulation time observed is wholly occupied by the action of thrombin on the fibrinogen. The time factor in the activation by kinase is negligible. These results suggest, perhaps, that the events in activisation are physicochemical rather than chemical; but they cannot at present be held to support the view of Howell, as the possible influence of antithrombin factors was not considered in Barrett's work. His quantitative study of thrombin activity does not support Howell. He finds that when the concentration

[9] *Amer. J. Physiol.*, 1916, **46**, 250; *A.*, i, 693.
[10] *Zeitsch. physiol. Chem.*, 1914, **89**, 22; *A.*, 1914, i, 219.
[11] *J. Biol. Chem.*, 1916, **24**, 111; *A.*, i, 298.
[12] *Biochem. J.*, 1915, **9**, 511; *A.*, i, 229.

of lime salts is properly adjusted, the coagulation process proceeds according to the equation

$$xy = nz,$$

when

x = the time taken for complete coagulation,
y = concentration of thrombin,
z = concentration of fibrinogen,
n = a constant.

In a series of papers by E. Hekma [13] we have the thesis supported that the fibrin of blood clot is in the condition of a reversible gel, which with proper treatment may be reconverted into a sol and again coagulated. Here again, apparently, is support for the physicochemical conception of coagulation. Hekma,[14] and also Howell,[15] have studied fibrin formation with the ultramicroscope. They agree that it may first appear in the form of ultramicroscopic needles having the optical properties of crystals.

No reference has yet been made in these Reports to the fact that adrenaline influences the coagulability of the blood. If it be added to blood which subsequently traverses the liver and intestines, the organs are so stimulated as to add something to the blood which increases its coagulability. This property comes into the picture of adrenal action as one specially directed to prepare the animal for emergencies.[16]

Anaphylaxis.

Between the agents which determine and control the events of blood coagulation and those concerned in the phenomenon of immunity there are probably close relations. We cannot tell which particular line of study among all those which deal with the reaction of the animal to the intrusion of substances foreign to its tissues is most likely to lead to the illuminating generalisations which are being sought. It is justifiable to believe, however, that a proper understanding of the extraordinary facts of anaphylaxis will make a real breach in our ignorance. Why does an infinitesimal dose of a particular protein, when it escapes the protective effects of digestion, so affect the tissues of an animal that, provided time is given for certain events to mature, the reception of a second dose becomes a fatal affair? What, in physicochemical

[13] *Biochem. Zeitsch.*, 1914, **62**, 161; **63**, 204; **64**, 86; *A.*, 1914, i, 754, 875 1013.

[14] *Ibid.*, 1916, **73**, 370, 428; *A.*, i, 447, 448.

[15] *Amer. J. Physiol.*, 1914, **25**, 143; *A.*, 1914, i, 1151.

[16] W. B. Cannon, W. L. Mendenhall, and H. Gray, *ibid.*, **34**, 225; *A.*, 1914, i, 765.

terms, does this "sensitisation" to particular proteins mean? How comes it that the reaction is at times so rigidly specific? Something of fundamental importance to biology resides in the answers to these questions.

The work recently described by H. H. Dale and P. Hartley[17] has shown that when the three types of protein obtainable from serum are carefully separated, each one can act as a distinct anaphylactic antigen. It has shown, moreover, that the sensitisation may, in the case of successful preparations, be perfectly specific, so that euglobulin, for example, produces sensitiveness to euglobulin and not to pseudoglobulin, whilst injection of albumin produces a high degree of sensitiveness to albumin and none to globulin. With pseudoglobulin preparations, such clear specificity was never observed; but as this fraction is by far the most difficult to purify, there is little doubt that when its injection sensitises more or less to the other fractions, it is merely because traces of these are still present. When it is remembered that 1/20,000 milligram of a particular protein may sensitise to that protein,[18] anaphylactic specificity may well be a very rigid test of the completeness of a separation. These observations fully illustrate the fact, now becoming familiar, that specificity in an antigen is not due to vague "biological" qualities, but to chemical or physico-chemical properties inherent in the antigen as a substance. The blood of an individual yields two or more proteins which prove to be distinct antigens, whilst homologous proteins from quite different species may prove indistinguishable. In the paper under discussion it is shown, for example, that the crystalline albumins in ducks' eggs are identical as antigens with those of the hen's egg. Such observations are not entirely new, but because of the excellent technique which the authors employed they add greatly to our confidence in the facts.

Upon what does antigenic specificity depend? We have now good evidence that albumins are chemically distinct from globulins,[19] but, so far as a balance in amino-acids is concerned, there would seem at least to be no difference between one class of globulin and another. It is, nevertheless, difficult to believe that antigenic distinctions could exist apart from the true chemical differences, and, as Dale and Hartley remind us, there is abundant room for such differences in the order of the linkings, even in the case of two proteins with identical amino-acid content.[20]

[17] *Biochem. J.*, 1916, **10**, 408; *A.*, i, 859.

[18] H. G. Wells, *J. Infect. Dis.*, 1908, **5**, 449.

[19] P. Hartley, *Biochem. J.*, 1914, **8**, 541, *A.*, 1914, i, 1206; also C. Crowther and H. Raistrick, *ibid.*, 1916, **10**, 434; *A.*, i, 864.

[20] H. W. Dudley and H. E. Woodman, *ibid.*, 1915, **9**, 97; *A.*, 1915, i, 468.

The results of the research just discussed will be found to have practical bearings in connexion with the concentration of antigens in the therapeutic sera. The hæmoglobins from the blood of different animals show marked specificity as anaphylactic antigens.[21]

H. G. Wells[22] has shown that the so-called β-nucleoproteins, which are compounds of guanylic acid with protein, and can be extracted from organs with boiling water, possess definite antigenic properties demonstrable by the anaphylaxis reaction. As there are but few known proteins which retain their antigenic capacity after boiling, the observation may give some indication as to the nature of the protein moiety of these substances.

Needless to say, many theories to account for the facts of anaphylaxis have already been advanced. I will refer very briefly to a recent one which does not introduce any especially new conception, but will illustrate the trend of thought. It relates with anaphylactic phenomenon some of the newer facts which I have discussed in connexion with blood coagulation.

It was pointed out that treatment with chloroform not only causes plasma to coagulate, but confers toxicity on serum. This action is associated with a destruction of antitrypsin, and with a consequent increase in the proteolytic power of the serum. It is conceivable, therefore, that the toxicity gained by the serum is due to the formation of fission products from its proteins. Now the occurrence of an interaction between an antigen and its anti-substance affects the colloid equilibrium in circulating blood in such a way as to diminish its antitryptic properties. In anaphylaxis, the first, or sensitising, dose of a foreign protein produces an anti-substance, the excess of which continues to circulate. When the second dose of antigen is injected, the interaction with its anti-substance occurs, and simultaneously the antitryptic power of the blood is lowered. As a result, toxic fission products are produced by the action of trypsin on the proteins of the blood, and these are responsible for the anaphylactic shock.

This, stated very briefly, is the view put forward by J. Bronfenbrenner.[23] The theory of this author has more originality, but is less easy to follow, when he extends it to bring the facts of passive immunity into relation with those of anaphylaxis. I must not, however, give space to this extension here. There is some consensus of opinion in favour of the view that it is protein disintegration products formed *in vivo* which produce the remark-

[21] H. C. Bradley and W. D. Sansum, *J. Biol. Chem.* 1914, **17**, xxviii; *A.*, 1914, i, 617.

[22] *Ibid.*, 1916, **28**, 11.

[23] *Proc. Soc. expt. Biol. Med., New York*, 1915, **13**, 19; *A.*, i, 181.

able symptoms of anaphylactic shock, although of their nature we are as yet ignorant. On the other hand, it is generally held that only an intact protein can act as the antigen or sensitiser. The claim has recently been made[24] that it is possible to render rabbits anaphylactic by injecting so simple a substance as diglycylglycine. Several injections have to be made in order to sensitise the animal. A final dose given after a longer interval than those which intervened between the sensitising injections produced a moderate fall of blood pressure, with some acceleration of respiration and of intestinal movements. These symptoms are, it is true, part of the picture of anaphylactic shock. They are of very mild degree, however, and I think it doubtful if the evidence given by the experiments as a whole can be taken as showing that true anaphylaxis can be produced by the tripeptide.

The Hydrolysis of Proteins: Tissue Autolysis.

Many details in the hydrolytic decomposition of proteins are still obscure, and require to be cleared up for the sake of both chemical and physiological knowledge. In the case of acid hydrolysis, for instance, destructive changes occur which are not yet fully understood. A part of the nitrogen of the protein passes into the so-called "humin" fraction, which consists of dark, amorphous products containing always an appreciable percentage of the original protein nitrogen. These products call for study, because there has long been evidence that they are in some way related to natural melanotic pigments, and also because their formation introduces uncertainty into quantitative work on amino-acids as produced by acid hydrolysis. It has been shown, for example, that any attempt to apply Van Slyke's amino-nitrogen determination directly to the analysis of feeding-stuffs breaks down, owing to the large and irregular yields of humins on hydrolysis.[25]

The complete destruction of tryptophan which occurs when protein is boiled with acid turned attention to the possibility that the indole nucleus was concerned in humin formation. R. A. Gortner and M. J. Blish[26] found that whilst zein yields very little humin when hydrolysed alone, a considerable amount is formed if tryptophan is added. The yield of humin from protein is always increased when carbohydrates are present, and the authors quoted shows that when tryptophan is mixed with carbohydrates and boiled with acid, nearly 90 per cent. of its nitrogen is

[24] E. Zunz and (Mlle.) Diakonoff, *Biochem. J.*, 1916, **10**, 160 ; *A.*, i, 528.

[25] H. S. Grindley and M. E. Slater, *J. Amer. Chem. Soc.*, 1915, **37**, 2762 ; *A.*, 1915, ii, 598.

[26] *Ibid.*, 1630 ; *A.*, 1915, i, 726.

recovered in "humin." They suggested that the reaction involved in humin production was the condensation of an aldehyde with the imino-group of the tryptophan nucleus, a type of reaction previously studied by Miss A. Homer.[27] H. S. Grindley,[28] however, showed later that tryptophan-free zein increased its humin–nitrogen from 0·56 to 1·84 per cent. when hydrolysed in the presence of dextrose, and suggested that other amino-acids besides tryptophan must share in nitrogenous humin formation. Gortner[29] has since admitted this. A recent paper by M. L. Roxas[30] confirms the fact, however, that tryptophan takes by far the largest share in the process. When boiled with 20 per cent. hydrochloric acid plus sugar, the following amino-acids yielded humin, whilst the proportion of their nitrogen concerned in the formation was: tryptophan, 71·0; tyrosine, 15; cystine, 3·1; arginine, 2·33; lysine, 2·62; histidine, 1·84 per cent. In the case of tryptophan, arginine, and histidine, the amino-group is concerned in the condensation which occurs, but with tyrosine and cystine another group seems to be involved.

Another point of practical interest to protein studies is the question whether it is possible to produce a complete liberation of all the amino-acids by the action of enzymes *in vitro*. Abderhalden has long claimed,[31] and still claims,[32] that by the successive and prolonged action of pepsin, trypsin, and erepsin, protein is completely broken down. He has continued to use for feeding experiments preparations so made, on the assumption that they are free from polypeptides. This position has been challenged by Henriques[33] and his co-workers. A. C. Andersen[34] has recently published papers bearing on the matter. According to him, it is extremely difficult, if not impossible, to reach with the enzymes a degradation so complete that subsequent treatment with acid produces no further changes in the products. He finds that after very prolonged zymolysis the end-products still yield, when boiled with acids, a further quantity of free amino-groups and also a noteworthy proportion of extra free ammonia. The fact that this ammonia is liberated by acid, and not by enzymes, suggests that it is derived from some special groupings in the protein molecule, and the author thinks that uramido-groups are its most probable

[27] *Biochem. J.*, 1913, **7**, 116; *A.*, 1913, ii, 451.
[28] *J. Amer. Chem. Soc.*, 1915, **37**, 1778, 2762; *A.*, 1915, ii, 598; 1916, ii, 119.
[29] *J. Biol. Chem.*, 1916, **26**, 177; *A.*, i, 681.
[30] *Ibid.*, **27**, 71; *A.*, i, 797.
[31] See E. Abderhalden and P. Rona, *Zeitsch. physiol. Chem.*, 1907, **52**, 508.
[32] *Ibid.*, 1915, **96**; i, 147; *A.*, i, 580.
[33] *Ibid.*, 1913, **88**, 361.
[34] *Biochem. Zeitsch.*, 1915, **70**, 344; *A.*, 1915, i, 1015.

source. E. M. Frankel[35] has also published a recent elaborate study of the rate of decomposition of various proteins under the influence of the three digestive enzymes acting separately or consecutively. He did not follow digestion to its final equilibrium, however, but he obtained by the consecutive action of all three ferments a liberation of as much as 85 to 90 per cent. of the amino-nitrogen in a period of seventeen to eighteen days. If, as Andersen suggests, there are really groups in the protein molecule which the known enzymes of the digestive tract are unable to liberate, the point is one of interest. Otherwise the apparent differences in the experience of different workers may be due merely to variations in their technique.

In connexion with proteolysis by enzymes, reference must be made to the remarkable statements of E. Herzfeld,[36] who claims to have shown that the cleavage products of protein have themselves proteolytic properties. According to him, the activities of pepsin preparations are largely due to proteoses and those of trypsin to amino-acids, whilst even pure amino-acids have a proteolytic action.

Now it has been shown by others that the typical curve of the velocity of trypsin action differs from a logarithmic curve in that it gradually falls away from such a curve owing to the retarding influence of the products of cleavage, especially amino-acids.[37] There is no evidence of autocatalysis such as Herzfeld's claims would call for. Indeed, the theoretical difficulties involved in his statements are such that one is compelled to look critically at the experimental evidence on which they are based. In my opinion this is not by any means convincing, and I am not surprised to find that criticism is already beginning to make itself felt in the literature.[38] Some of the observations chronicled by Herzfeld call, nevertheless, for explanation, and his papers should receive attention from other workers.

It has recently been claimed by M Morse[39] that the degradation of proteins in tissue autolysis is an autocatalytic phenomenon. A certain grade of acidity has long been known to favour the process, and the author mentioned has found that if the rate of increase of hydrion concentration which occurs during the autolysing of a tissue be plotted, it yields a curve of the logarithmic type, closely following the curve of proteolysis in the same tissue.

[35] *J. Biol. Chem.*, 1916, **26**, 31 ; *A.*, i, 682.

[36] *Biochem. Zeitsch.*, 1915, **68**, 402, *A.*, 1915, i, 468 ; *ibid.*, 1915, **70**, 262 ; *A.*, 1915, i, 1019.

[37] W. M. Bayliss, *Arch. Sci. Biol. St. Petersburg*, 1904, **11**, Suppl. 281 ; *A.*, 1905, ii, 267.

[38] C. Funk, *J. Biol. Chem.* 1916, **26**, 121 ; *A.*, i, 767.

[39] *J. Biol. Chem.*, 1916, **24**, 163 ; *A.*, i, 299.

He writes: "When we remember that the development of acidity is the *sine qua non* for autolysis, we have reason to believe that the process is an autocatalytic one, the developing acidity inducing greater and greater acceleration in the digestion rate, and when the acid reaches a maximum in its production, digestion likewise reaches its maximum." In commenting on this paper, H. C. Bradley[40] truly remarks that, since proteolysis is in question, the conclusion would really seem to affirm that the products of this —proteoses, amino-acids, etc.—accelerate the change, although, doubtless, this was not intended by Morse. It is clear, moreover, that none of the curves brought forward shows, as a matter of fact, the slightest indication of acceleration in the *rate* of digestion. The term autocatalysis is therefore entirely misleading. True, the formation of acid within the tissue activates the autolytic enzymes, and in this sense the tissue, considered as a whole, initiates the degradation of its proteins; but when taking even this point of view, it has to be remembered that the acidity (due to lactic acid) is not produced in the process of proteolysis, but on quite other lines, so that in no sense have we to deal with autocatalytic reactions.

In some experiments carried out by Bradley himself,[41] and by Bradley and Morse conjointly,[42] the interesting fact was brought to light that manganous chloride greatly accelerates liver autolysis. Moreover, whilst normally only 25 per cent. of the liver protein is affected, in the presence of the salt 75 to 90 per cent. is digested. Of the total liver proteins, those from the connective tissues are not attacked by the proteases present; hæmoglobin and albumin are only attacked when accelerating agents are added, whilst globulins are readily and completely digested. Manganous salts, it is suggested, so alter the resistant proteins as to render them vulnerable to the ferments. Bradley[43] considers this view to be confirmed when, in later work, he was able to show that an increase in the concentration of substrate, brought about by the addition of extraneous proteins, also produces acceleration. The fact that the liver proteases can digest foreign proteins was used in an ingenious manner to throw light on the mechanism of autolysis. The digestion rate of the liver proteins themselves is closely related to hydrion concentration, progressive increase being observed from $P_H = 7{\cdot}4$ to the optimum acidity (measured in a dialysate) of $P_H = 6{\cdot}0$. The rate of digestion of the foreign

[40] *J. Biol. Chem.*, 1916, **25**, 201; *A.*, i, 582.
[41] *Ibid.*, 1915, **20**, xxix; *A.*, 1915, i, 619.
[42] *Ibid.*, 1915, **21**, 209; *A.*, 1915, i, 619.
[43] *Ibid.*, 1915, **22**, 113; *A.*, 1915, i, 1028.

proteins, caseinogen and peptone, for instance, is, however, not affected by acid in a similar manner, and the effect of the acid cannot therefore be due to an activation of enzymes.

The true autolysis, involving the proteins of the organ itself, may also be almost inhibited by the addition of a salt, which actually accelerates the degradation of added caseinogen.[44] The action of acids, including carbonic, is therefore on the substrate, not on the proteases. It is suggested that the liver cell itself contains two classes of proteins, namely: (1) available proteins or those capable of being broken down by autolytic enzymes, and (2) resistant or reserve proteins. The equilibrium between these is dependent on the concentration of hydrogen ion in the cell at any moment. A working hypothesis is based on these conclusions and applied to such occurrences in the body as involve autolysis and tissue destruction, or the reverse processes which occur in hypertrophy. Atrophy, involution, and necrosis are preceded by a local asphyxia, which induces increase of acidity. Hypertrophy is, as a rule, conditioned by an increased blood supply, which, by securing removal of carbon dioxide and the oxidation of organic acids, as well as by constantly renewing the supply of the phosphate buffers from the blood, reduces autolysis to a minimum. The "available" proteins thus tend to be converted into the reserve type, and with increased synthesis of the former the cell proteins tend to increase to a maximum. Simple hypertrophy results. Such a contribution to our conceptions of cell equilibrium is, at any rate, worthy of attention.

The Importance of Individual Amino-acids in Nutrition.

This subject was dealt with in the lecture which I delivered before the Chemical Society last May. When that lecture was given, I was ignorant of the long paper Abderhalden published during the year 1915. No abstract of this appeared in the Journal of the Chemical Society until August, 1916, and I had myself had no access to the journal in which it appeared.[45] The paper, however, although comprising a discussion of considerable length on the special subject of this section, contributes but little to the actual facts. It contains further weighty evidence to show that the animal is able to deal with the total amino-acids of completely predigested protein, for it describes the successful nutrition of a dog for no fewer than 290 days on such material derived from various sources. A second dog flourished on similar material

[44] H. C. Bradley and J. Taylor, *J. Biol. Chem.*, 1916, **25**, 261, *A.*, i, 582.
[45] *Zeitsch. physiol. Chem.*, 1915, **96**, 1; *A.*, i, 580.

for 147 days. The experiments, on the other hand, in which the nutritive importance of individual amino-acids was tested were in most cases inconclusive.

That many workers should be independently engaged on a study of this question is not surprising, for all must recognise its interest.

Two methods of determining the nutritive importance of this or that protein constituent have been used. The one consists in removing individual amino-acids from the total products of hydrolysis and feeding animals on the residuum. This was first employed, although with imperfect technique, by Henriques and Hanson in 1905. It has been largely used by Abderhalden. The other method has been employed in the admirable experiments of Osborne and Mendel, by McCollum and Davis, and by some others. It consists in feeding with pure proteins in which, with some degree of accuracy, the amino-acid balance is known. The effect on nutrition of deficiency or excess of a given constituent can be thus observed. Each method has its advantages and its obvious limitations.

Another distinction in method must be mentioned. The nutritive effect may be observed in the gain or loss of body-weight, or changes in the nitrogen balance of the animal may be registered. The latter method has traditional support, and to some minds it represents the one indispensable test of nutritional success. To the study of some aspects of metabolism, information concerning nitrogenous equilibrium is, of course, essential, but in connexion with experiments of the type now under discussion it is frequently unnecessary, and, as a test, it may be, I think, even misleading. The objection to relying on body-weight changes is that they may not concern the essential tissues, but represent merely gain or loss of fat, or even of water. No such criticism is jstifiable, however, if the experiment is reasonably prolonged. The fact that the nitrogen balance has been determined is sometimes made to excuse the shortness of an experiment. In such short studies, however, the determination may itself mislead. A negative balance induced by the omission of a constituent from the diet after a control period showing equilibrium may, if of a comparatively brief duration, represent no more than a period of adjustment. The nitrogen balance is a safe indication of quantitative deficiencies in the total energy supply, but unless it be followed for considerable periods it is a less safe guide as to the real and permanent importance of some qualitative change in the diet. I think that this objection applies to certain of Abderhalden's experiments. It should be pointed out, however, that in the paper under notice he himself

repudiates a blind trust in the factor of nitrogenous equilibrium.[46] Abderhalden contributes further evidence to show that tryptophan is indispensable, a fact on which all observers are agreed. He finds that the (not wholly complete) removal of tyrosine produces at once a negative nitrogen balance in the animal, but that phenylalanine can, at least partly, replace the tyrosine. In this connexion, it is to be noted that G. Totani[47] obtained prolonged maintenance of his animals, and even some growth, after removing tyrosine as completely as possible. Even when hydrolysed gelatin with added tryptophan was given, maintenance was satisfactorily accomplished. Totani concluded that the functions of tyrosine were being subserved by phenylalanine, and believed, further, that the animal has some power of synthesising orthocyclic amino-acids. H. H. Mitchell[48] has also published experiments suggesting that the orthocyclic acids are not altogether indispensable. With regard to other amino-acids, Abderhalden's experiments—at least up to the date of the 1915 paper now under notice—supply no satisfactory information. He found, for instance, that the removal of lysine, of arginine, or of histidine left the amino-acid mixture without any power of maintenance, but unfortunately in none of these cases was that power restored when the missing amino-acid was replaced. From this circumstance, it was concluded that the process of removal had in some way altered the nature of one or other of the remaining constituents. This was not at all the experience of H. Ackroyd and myself.[49] By a careful application of Kossel and Kutscher's method to the hydrolysis mixture, we removed arginine and histidine together, and afterwards replaced one or both. It was easy to show that in the absence of both there was nutritional failure, and restoration when both were replaced. In our experiments, however, the fact came to light that either one of these two protein constituents can to a large degree serve vicariously for the other.

Abderhalden draws the interesting conclusion that proline is not indispensable. In the case of cystine and glutamic acid, the only other units investigated, his results were inconclusive. With regard to the former of these two, there can be little doubt, however, that it is essential, not only because it carries the sulphur of protein, but from general evidence already available. F. W. Foreman and I[50] have obtained results which at least suggest that glutamic and aspartic acids can be dispensed with.

[46] *loc. cit.*, p. 51.
[47] *Biochem. J.*, 1916, **10**, 382 ; *A.*, i, 860.
[48] *J. Biol. Chem.*, 1916, **26**, 231 ; *A.*, i, 690.
[49] Paper in the press ; *Biochem. J.*, **10**.
[50] Lecture ; *T.*, 1916, **109**, 639.

Studies based on the removal of individual amino-acids from the food are only now beginning; I am sure they will ultimately yield very valuable information.

In observations described in the paper already referred to, H. H. Mitchell adopted the plan of feeding with mixtures of pure amino-acids. Such diets are, of course, very costly, and at the present time impossible to prepare in considerable quantities. The experiments were therefore confined to mice. The chief conclusion indicated, apart from that concerning the relatively small importance of tyrosine, is that, except in the case of preparations free from tryptophan, there is little difference—as judged by the rate of decline in body-weight and the survival period—in the nutritive effect of mixtures of very varying composition. The mixtures supplied were, of course, never complete, and their amount was usually quantitatively insufficient. In a general discussion, this author refers to the "suggestive theory of Osborne and Mendel to the effect that the only reason for the destruction of any protein at all in maintenance might be to liberate a small amount of one or two, or at most a relatively small number, of amino-acids to engage in some 'hormone-like physiological duty upon which proper metabolism might depend,'" whilst the view that "at least some of the amino-acids have specific functions in metabolism, aside from that of serving simply as material for the synthesis of body protein," is referred to as "recently and tentatively put forward by Osborne and Mendel." I may be permitted to point out that this theory, and no less the view, were explicitly put forward more than ten years ago.[51]

Osborne and Mendel[52] have brought forward further evidence to show that the nutritive value of lactalbumin is superior to that of caseinogen, a circumstance of practical importance, depending doubtless on the balance of amino-acids characteristic of these proteins. Edestin is inferior to either of the milk proteins.

When the protein supply was cut down to a minimum, it was found that to produce the same gain in body-weight "50 per cent. more casein than lactalbumin was required, and of edestin nearly 90 per cent. more." In other experiments it was found that with approximately equal intakes of total food there was an equal gain of weight when lactalbumin formed 8, casein 12, and edestin 15 per cent. of the dietary. The addition of cystine, equivalent to 3 per cent. of the casein employed, made that protein much more efficient. The same authors have also published further experiments on the effects of adding tryptophan and lysine to zein. The

[51] F. G. Hopkins, *Science Progress*, New Series, Vol. I, No. 1, July, 1906; Miss E. G. Willcock and F. G. Hopkins, *J. Physiol.*, 1906, **35**, 88.

[52] *J. Biol. Chem.*, 1916, **26**, 1; *A.*, i, 690.

animal is maintained when the former is added alone, although not with the latter alone. When both are added there is growth. The quantities of these two amino-acids can be made the limiting factors which determine nutritive equilibrium and the possibility of growth. They afford an illustration of the "law of the minimum" as applied to the food supply of an animal.

That lysine is necessary for growth is shown in the experiments of others.[53] It seems to me entirely wrong, however, to speak of this diamino-acid as though it were a special growth factor or as "stimulating" growth. It is, like tryptophan and some other protein units, material which the animal cannot synthesise for itself, and, being a tissue constituent, it must therefore be present in the food.

The Residual Nitrogen of the Blood.

I. Bang has published a long series of papers on the residual, or non-protein, nitrogen in the circulating blood of man and of various animals. Some of the results given are not altogether in accordance with those obtained by others, and some are puzzling, but the work of so experienced an experimentalist on so important a subject calls for attention.

The methods used were the author's own. I am unable to appraise them, as they have been described only in a monograph published at Wiesbaden during the war. The urea nitrogen and the amino-acid nitrogen were separately determined. The former varies between 6 and 20 milligrams per c.c. of blood, with a mean of 12 milligrams; the latter between 3 and 22 milligrams, also with a mean of 12 milligrams.[54] These figures apply to human blood and to that of the ox, sheep, pig, and horse, all of which agree closely. Those for the rabbit are higher. In starvation,[55] the urea unexpectedly rises, but this effect is largely due to deficiency of water, and perhaps to some renal factor. Starvation has no effect on the amino-acid nitrogen, a circumstance which, although at first surprising, is in accordance with the observations of others. It indicates that there is a regulatory mechanism in tissue autolysis which maintains a definite equilibrium of circulating amino-acids. More remarkable and less in accordance with the statements of others is Bang's claim that a large meal of protein does not increase the amino-acid nitrogen, although it pro-

[53] G. D. Buckner, E. H. Nollau, and J. H. Kastle, *Amer. J. Physiol.*, 1915, **39**, 162; *A.*, i, 102.

[54] *Biochem. Zeitsch.*, 1915, **72**, 104; *A.*, i, 178.

[55] *Ibid.*, 119; *A.*, i, 178.

duces a brief increase in the urea. When free amino-acids are given,[56] an increase is observed, especially in fasting animals, about an hour after the administration. So far, the observations are reconcilable with current views concerning the digestion and absorption of proteins. Work was quoted in last year's Report to show how rapid are the processes of intermediate metabolism, and it may well be, in special circumstances at any rate, that with the comparatively slow absorption which goes on during normal digestion the amino-acids are dealt with rapidly enough to prevent any appreciable rise in their concentration in the blood. This need not remain true with the more rapid absorption of free amino-acids when directly administered.

Much more puzzling, however, are results which seem to show that a diminution of amino-acids in the blood, and even their disappearance therefrom, may occur after a large protein meal. There seems to be no explanation for this, and if Bang's observations are confirmed, we have an obscure phenomenon before us. I find certain other results[57] reported by him equally difficult to understand. As a consequence of giving glycine by the mouth to rabbits, an increase of amino-acid nitrogen in the blood was observed which, within certain limits of administration, was roughly proportional to the amount of glycine ingested. Equivalent quantities of leucine, however, produced no such increase. Its administration was followed, on the other hand, by a rapid rise in the urea of the urine. Leucine is more rapidly deaminised than glycine. These observations led to experiments in which a mixture of the above amino-acids, and also gelatin and certain proteins, were given. From the results as a whole, the conclusion is drawn that those proteins which on hydrolysis yield little or no glycine give rise on their ingestion to no increase in the amino-acids of the blood, whereas those yielding relatively large amounts cause a corresponding increase in the circulatory amino-acid. It is not difficult to understand that the acids of higher molecular weight may be more readily deaminised in the liver than is glycine. It is most difficult, however, to believe that, under normal conditions of absorption and metabolism, glycine alone among amino-acids should pass the liver unchanged. It is more easy to believe that glycine—which is but a small constituent of any tissue proteins save those of the stable connective tissues—is less rapidly dealt with by the tissues as a whole, and therefore remains longer in the blood.

That the tissues offer differential treatment to the various

[56] *Biochem. Zeitsch.*, 1915, **72**, 129 ; *A.*, i, 178.
[57] *Ibid.*, 1916, **74**, 278 ; *A.*, i, 579.

amino-acids is suggested by some experiments carried out by U. Lombroso.[58] In these, amino-acids, dissolved either in blood or in Ringer's solution, were perfused through isolated surviving organs. It was found, in agreement with Bang's results, that glycine was but little affected during passage through the liver. It was broken down in muscle, however. Alanine, on the other hand, is apparently less readily dealt with in the muscle than in certain other organs. The experiments of this author further indicate that an important difference exists between blood and salt solutions as perfusion media. When Ringer's solution was used, the disappearance of amino-acids during perfusion was associated with evidence of deamination and oxidation. When blood was employed there was, in the opinion of the author, more evidence for the occurrence of synthesis.

The Sugar of the Blood.

Some three years ago I. Bang published an account of his researches on blood sugar in the form of a separate monograph.[59] Among matters of interest brought forward in the book was evidence to show that the liver itself deals with a smaller proportion of the sugar ingested at any time than we have been apt to suppose. Estimations in the blood showed that during the absorption of a carbohydrate meal a large amount of sugar escapes the liver. It would seem that we must credit the tissues as a whole with considerable power of storing carbohydrate in one form or another. G. Graham[60] has supported such a view with the results of experiments carried out on himself. He makes the interesting suggestion that when the body is fatigued there is a lessened ability to store carbohydrate, so that under conditions of fatigue the rise of blood sugar which results from a given ingestion is considerably above the normal.

U. Lombroso[61] has investigated the fate of blood sugar under experimental conditions which are more or less new. Some of his results call for critical attention. He maintains that an explanation for the contradictory results which have been reported concerning the fate of sugar in shed blood is to be found in the circumstance that a synthetic condensation of the dextrose in the blood, as revealed by the experiments of Levene and Meyer, occurs

[58] *Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 401 ; *A.*, i, 101 ; compare *ibid.*, **24**, i, 1253 ; *A.*, 1915, i, 917.

[59] "Der Blutzucker," Wiesbaden, 1913.

[60] *J. Physiol.*, 1916, **50**, 285 ; *A.*, i, 613.

[61] *Atti R. Accad. Lincei*, 1916, [v], **25**, i, 736 ; *A.*, i, 612 ; *ibid.*, 802 ; *A.*, i, 686 ; *ibid.*, ii, 41 ; *A.*, i, 686 ; *ibid.*, 83 ; *A.*, i, 770.

at the outset, but if the blood is allowed to remain longer, this is followed by a degradation of the complex, and subsequent destruction of the liberated sugar. The synthetic function and the glycolytic function are independent variables. If blood with added sugar is circulated through the pancreas or intestine, there is an increase in its glycolytic power, with little or no change in its power to condense the sugar. If, on the other hand, fresh blood poor in sugar is first circulated through the same organs, and sugar is subsequently added to it, a marked increase in the synthetic power is observed, the glycolytic power being scarcely affected. The blood of a depancreatised dog has little glycolytic capacity, but its power to condense sugar remains almost normal.[62] If it is circulated through the intestine of the animal from which it was taken, it gains greatly in the glycolytic factor. Clearly the most striking of this author's claims are those relating to the influence of the intestine. The gut yields a glycolytic agent, or, in other circumstances, a condensing agent, to the blood. It yields them even more readily than the pancreas. Some of these results seem to me quite inexplicable at present, but that the intestinal epithelium might have to be classed among the tissues specially concerned in carbohydrate equilibrium has always been probable.

Renal Permeability.

The present availability of methods which permit of the estimation of blood constituents in very small quantities of material has encouraged activity in various fields. Many, for instance, have been engaged on investigations concerning the permeability of the kidney. Physiologists want to know how far the excretion of this or that urinary constituent is dependent on its concentration in the blood, and whether the rate of excretion is controlled by differences of concentration in the blood and urine respectively. Does the normal kidney display a constant "permeability" when such factors are constant? If so, and if a measure of normal permeability can be established, pathologists require to know how this permeability varies in disease. This is, of course, very far from being a new region for research, but work on it has gained impetus now that accurate estimations can be made in the circulating blood without inconvenience to the subject of experiment.

A few years ago Ambard and Weil[63] asserted that in the case of urea such relations hold that with a given concentration in the urine the rate of its secretion varies as the square of its concen-

[62] Compare H. McLean, *J. Physiol.*, 1916, **50**, 168; *A.*, i, 613.
[63] *J. Physiol. et Path. gén.*, 1912, **14**, 753.

tration in the blood, whilst with a given concentration in the blood the rate varies as the square root of the urinary concentration. These relations, as obtained by experiment, they combined in a formula, which is mostly used in the form:

$$\frac{\text{Concentration in the blood}}{\sqrt{\text{Rate of excretion}}} = \text{constant.}$$

They found this to hold in a great number of normal people under very varying conditions. Any considerable departure from it was taken as an indication of renal abnormality. These claims have been supported by others.[64]

During the present year, however, T. Addis and C. K. Watanabe[65] have criticised Ambard and Weil's law of excretion. It is common to find in physiology that, once a "law" is promulgated, its limitations begin to come to light. The authors just quoted find that factors other than the concentration of urea are important in determining the rate of its excretion by the normal kidney. They found, it is true, in thirty-nine experiments done upon young healthy adults that when the conditions are the same the organ displays a high degree of constancy of function.[66] Large doses (24 and 40 grams respectively in different experiments) of urea were given by the mouth, and the rate of its excretion followed in successive periods after the administration. This rate was remarkably constant both when different individuals were compared and also in the same individual on different occasions. The excretion rate, however, was in each case lower in the earliest hours of the experiment, when the concentration in the blood was directly shown to be at its highest, than in the immediately succeeding periods with less in the blood. The kidney is not passive. The successive administration of identical doses of urea proved, from the identity of the excretion rate following each dose, that "kidney fatigue" could not be induced under the conditions of these experiments. This leads me to refer once more to one of I. Bang's[67] papers. This author, finding that after giving urea to rabbits there was a somewhat prolonged display of excess in the blood, came to the conclusion that the kidney was fatigued by the extra calls made on it. He gave very large

[64] Compare F. C. McLean and L. Selling, *J. Biol. Chem.*, 1914, **19**, 31; *A.*, 1914, i, 1183. Also F. C. McLean, *Amer. J. Physiol.*, 1915, **36**, 357; *A.*, 1915, i, 186.

[65] *J. Biol. Chem.*, 1916, **24**, 203; *A.*, i, 352.

[66] *Ibid.*, **27**, 249; *A.*, i, 864.

[67] *Biochem. Zeitsch.*, 1915, **72**, 139; *A.*, 1915, i, 179.

doses, however, apparently about 5 grams per kilo., and for this reason his results are less important in their bearing on the very interesting question of physiological renal fatigue. His doses were large enough, indeed, to prove very poisonous to the animals. He ascribes the effects to ammonia poisoning, having found that ammonia is largely increased in the blood as the result of giving urea. This observation is interesting in its suggestion that the reaction by which urea normally is formed from ammonium salts is reversible. It is not easy, however, to reconcile Bang's findings with certain other experimental facts, for B. C. P. Jansen [68] has recently confirmed the earlier results of Wakeman and Dakin [69] in showing that perfusing the liver with blood containing ten times the normal concentration of urea leads to no ammonia formation. The normal reaction by which urea is formed from ammonium salts seems, therefore, to be irreversible under these conditions. In parenthesis, I may point out that although creatinine is formed from the creatine of muscle, W. C. Rose and F. W. Dimmitt [70] have shown that a large increase of the former in the blood leads to no increase of the latter in the muscles. This reaction again seems to be irreversible. No one, I think, has yet observed the reversal of either of these reactions under the control of suitable enzymes. It would be most interesting to know in every such case how far the apparent irreversibility is inherent in the reaction and how far the properties of the living cell intrude in the matter.

Having regard to the results just quoted, it is difficult to understand how and where the large ammonia formation from circulating urea could have occurred in Bang's experiments.

Returning to the subject with which this section is more particularly concerned, I may direct attention to the interesting observations of V. C. Myers, M. S. Fine, and W. G. Lough,[71] which show that whilst in the early stages of clinical nephritis uric acid is the excretive which chiefly accumulates in the blood, at later periods, when the permeability of the kidney has further decreased, urea accumulates and then creatinine. When the disease nears the fatal stage, the amount of the last-mentioned excretive found in the blood may be twenty times the normal. Severe nephritis may markedly reduce the permeability of the kidney to dextrose and upset any normal relation between the sugar in the

[68] *Arch. Néerland*, 1915 [iii B], **2**, 594; *A.*, i, 299.
[69] *J. Biol. Chem.*, 1911, **9**, 327; *A.*, 1911, ii, 629.
[70] *J. Biol. Chem.*, 1916, **26**, 345; *A.*, i, 774.
[71] *Proc. Soc. expt. Biol. Med., New York*, 1915, **13**, 5; *A.*, i, 192.

blood and urine. In diabetes, for instance, when the disease is complicated by nephritis, a given concentration of sugar in the urine may correspond with a much higher concentration in the blood than it would indicate in a case free from such renal changes. The renal permeability for sugar may vary considerably, however, without the existence of actual nephritis, as many papers dealing with the raising or lowering of the "leak-point" in diabetes have shown.[72]

F. Gowland Hopkins.

[72] See G. Graham, *Proc. physiol. Soc.*, 1915, xlvi.; *A.*, i, 1915, i, 1036.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

Although there has been a decided falling off in the rate of publication of some of the Continental journals, the number of papers published in 1916 does not show any very considerable reduction, owing, to a great extent, to increased activity in the United States.

The obituary list includes the well-known name of E. W. Hilgard, who for more than forty years held the positions of Professor of Agriculture and Director of the Experiment Station of California.

Among new publications may be mentioned a monthly journal, *Soil Science*, edited by J. G. Lipman; "Organic Agricultural Chemistry," by J. C. Chamberlain; "Beiträge zur Kenntniss der Ernährung der Zuckerrübe," by J. Stoklasa and A. Matousek; and "Die Kalirohsalze, ihre Gewinnung und Verarbeitung," by W. Michels and C. Przibylla.

The Atmosphere.

The Committee for the Investigation of Atmospheric Pollution have issued their first report,[1] for the year ending March, 1915, which contains the results of monthly analyses of rain-water made at twelve places for a whole year, and at a number of other places for shorter periods. The positions selected were, naturally, mainly in the largest towns. Malvern and Exeter were, however, included, and at these places it was found that the nitrogen in the form of ammonia amounted to only 1·9 kilograms per hectare per annum, the lowest yearly result hitherto recorded in England. At Malvern, the sulphates are unexpectedly high, the yearly amount per hectare being 50·5 kilograms, as compared with 19·5 kilograms at Rothamsted. The analyses are very complete, everything of importance being included, with the exception of nitrates, the exclusion of which, no doubt unavoidable, is to be regretted, as the figures would have been a useful check on the ammonia results.

[1] *Lancet*, Feb. 26, 1916, **190**, Suppl.; *A.*, i, 592.

In connexion with the results found at Sheffield, it has been pointed out[2] that the contamination of the air is at its worst on calm, foggy days when no rain is falling, and that on such occasions the method employed fails to give any record. That, however, will depend on the length of the periods without rain and on other atmospheric conditions. If the fog is blown away before the rain comes, the impurities which it contains will, of course, be lost; the fog may, however, be followed by showers, in which case a fairly good indication of the extent of the contamination will be obtained. In rainy weather, the greater part of the smoke (much of which is rapidly distributed over the surrounding country in fine weather) will be brought down by the rain as soon as it leaves the chimneys, so that, with the rainfalls of the various districts concerned, it is perhaps more likely that the rain-water results indicate too much contamination rather than too little.

Analyses of the air itself would add considerably to the value of the rain-water results, even if only three or four constituents were estimated.

In California,[3] an investigation of the atmosphere, in which nearly five thousand estimations of sulphur dioxide were made at two stations in a smelter zone, showed that the air may, under exceptional conditions, contain as much as 7·1 per million, and that even in San Francisco the amount of sulphur dioxide may reach nearly 2 per million. The average amount, calculated from all the observations, was, however, only 0·22 per million, whilst the average, under conditions favourable for high contamination, was 3·6 per million.

Analyses of rain-water have also been made at Mount Vernon, Iowa,[4] at St. Croix,[5] and at Montevideo.[6]

Soils.

A new kind of clay, having unusual properties, has been discovered in some unreclaimed land near the city of Mexico.[7] A few grams of the soil, which looks like an ordinary dark grey clay, placed in a 50 c.c. cylinder with some water, swelled very rapidly, and was found the next day completely to fill the cylinder. An analysis of the clay showed that it contains very little aluminium

[2] W. P. Wynne, "Rep. to the Health Committee of the Sheffield City Council," 1914–15.

[3] J. A. Holmes, E. C. Franklin, and R. A. Gould, *U.S. Bur. Mines, Bull.* 98, 1915.

[4] B. Artis, *Chem. News*, 1916, **113**, 3; *A.*, i, 304.

[5] L. Smith, *Rep. Agric. Exper. Stat. St. Croix*, Copenhagen, 1915.

[6] Schroeder, *Exper. Stat. Record*, 1916, **34**, 15.

[7] E. W. Hilgard, *Proc. Nat. Acad. Sci.*, 1916, **2**, 8.

in relation to the silica, and that the predominating base is magnesium. The soil, which was originally supposed to be afflicted with "alkali," contains comparatively small amounts of sodium sulphate and carbonate; it contains a good deal of calcium carbonate, and cannot therefore be reclaimed by liming, so that acid treatment would seem to be the only possible effective agent.

It is suggested that the material may be of practical use in closing the crevices in oil wells which are liable to flows of water.

Experiments on the flocculation of soil colloidal solutions showed that the effect of the same electrolyte varied considerably according to the composition of the soils, solutions from clay soils flocculating most readily, then loam soils, and lastly peat.[8] Quantitative experiments, in which the different soil solutions were brought to the same concentration (100 c.c. = 0·027 gram), showed that lead salts acted better than ferric sulphate and aluminium potassium sulphate, and that the minimum amount of electrolyte required was nearly the same with the best coagulants, lead nitrate and acetate and mercurous nitrate, whilst with other salts the amounts were very variable. Organic matter has a considerable effect on the stability of the colloid solution, five times as much N/5-nitric acid and seven times as much saturated calcium hydroxide solution being required in the case of peat as with clay, whilst with a mixture of clay and peat there is a regular rise in the amount of electrolyte required as the proportion of peat to clay is increased. Colloid solutions when diluted with water require less electrolyte for flocculation; the decrease is not, however, in proportion to the decrease in concentration.

Recent results in connexion with the question of the effect of climate on soils showed that Kansas and Maryland soils, when transferred to California for five years, became more deeply red in colour, and that Californian and Kansas soils were bleached to light grey or yellowish-grey in Maryland.[9] Samples of any one soil from the three stations were so changed as to become unrecognisable, and seemed to represent three very distinct types. As a rule, it was found that the numbers of bacteria, ammonification, nitrification, and fixation of nitrogen increased when arid soils were placed under humid conditions, and vice versa. The decomposition of cellulose, on the other hand, was always more rapid under arid than under humid conditions. Changes in composition were also observed; it was found that under arid conditions there is a tendency for iron to increase and for aluminium to decrease, whilst the change is reversed when Californian soils are transferred

[8] M. I. Wolkoff, *Soil Sci.*, 1916, **1**, 585; *A.*, i, 784.
[9] C. B. Lipman and D. D. Waynick, *ibid.*, 5.

to Kansas. Even without being moved, a soil may undergo considerable change in five years; in a Maryland soil the amount of magnesia was reduced from 2·3 to 0·21 per cent.

The increased loss of carbon under arid conditions would partly account for the decreased activity of the nitrifying and nitrogen-fixing organisms, and the former would be injuriously affected by unabsorbed ammonia and by organic matter dissolved by ammonia.

The fixation of phosphoric acid, dissolved from soils by dilute acids, which sometimes takes place when the extracts are left in contact with the soils, has been found to vary in extent according to the acid employed.[10] This might be explained on the assumption that the acid slowly decomposes aluminium or iron compounds, producing soluble salts, which react with the dissolved phosphoric acid; and the fact that with citric acid as the solvent employed the precipitation of phosphoric acid is less than with mineral acids would seem to support this view. It is, however, shown that not only phosphoric acid is taken up, but that oxalic acid is also withdrawn from its solution when left for a short time in contact with a soil in the presence of nitric acid. With 25 grams of a subsoil, 1 litre of $N/20$-nitric acid, and 0·094 gram of oxalic acid, about 82 per cent. of the oxalic acid was rendered insoluble, whilst with ten times as much oxalic acid about 25 per cent. was withdrawn from the solution.[11] Both oxalic and citric acids are more readily absorbed than phosphoric acid, whilst sulphuric acid is less absorbed, and hydrochloric and nitric acids not at all, or, at any rate, not appreciably. The withdrawal of acids from their solutions is attributed to adsorption by soil colloids, and is shown to follow the usual law. The order of the extent of adsorption of the different acids by soils is shown to agree with results obtained by Skraup with filter paper. The variations in the amounts of phosphoric acid taken up in presence of the different acids seems to depend on the relative adsorption of the acid solvent, so that with citric acid, which is readily adsorbed, the withdrawal of phosphoric acid is less than with nitric and hydrochloric acids, which do not seem to be adsorbed at all.

Until more is known as to the behaviour of plants towards adsorbed substances, it cannot definitely be said whether the availability of phosphoric acid in soils is more correctly indicated by results obtained after a short period of extraction or after more prolonged extraction—presumably the former, as phosphoric acid liberated by root action would probably not remain long enough in the soil to be adsorbed to any extent. This would correspond

[10] E. J. Russell and J. A. Prescott, *J. Agric. Sci.*, 1916, **8**, 65.
[11] J. A. Prescott, *ibid.*, 111.

with a diffusion method, which was found to give almost identical results with three different acids.

Some experiments in which a sandy loam was treated with a solution of potassium chloride (approximately $N/500$), and then leached with water, showed that the process of adsorption may be reversed, the water being more rapidly adsorbed than the dissolved salt, so that the concentration of the percolates was increased as compared with the original solution.[12]

Investigations on the solutions present in soils have usually been made with drainage or with soil extracts, which involve considerable dilution of the water originally present. A method has now been employed in which the soil water is separated from the soil by a pressure of 300 kilograms or more per sq. cm. In this way, sufficient amounts of solution can be obtained from soils containing considerable amounts of clay or organic matter.[13]

Analyses of some expressed solutions showed that the amount of calcium varies a good deal in the surface soil, but remains constant in the subsoil for a considerable part of the year. The amounts of potassium were always found to be lower in unmanured than in manured soils, and the movements of potassium were found to be analogous to those of calcium. The concentration of the soil solution, to a depth of 50 cm., is diminished by heavy rainfalls and increased by prolonged evaporation. Whilst the variations in the course of a year are considerable, the curves for potassium and calcium are remarkably similar, and seem rather to put out of court the accepted ideas with regard to the absorption of potassium.

Other experiments with expressed soil solutions have also given indications that the method is likely to be of value.[14] It has also been found that, in physical analyses of soils, the influence of manures and of season are clearly indicated when, instead of distilled water, a soil solution is employed. For this purpose, an artificial solution has to be used, owing to the large amounts required.

Analyses of drainage waters from lysimeter tanks, extending over five years,[15] have showed that applications of lime to the soil failed to liberate potassium, and crop results indicated that assimilation of potassium was not increased by lime. The amount of magnesium in the drainage was, however, increased; applications of potassium sulphate increased the calcium and magnesium, but not the potassium.

[12] A. G. McCall, F. M. Hildebrandt, and E. S. Johnston, *J. Physical Chem.* 1916, **20**, 51; *A.*, i, 304.

[13] E. Ramann, S. März, and H. Bauer, *Internat. Mitt. Bodenk.*, 1916, **6**, 1.

[14] J. P. van Zyl, *J. Landw.*, 1916, **64**, 201.

[15] T. L. Lyon and J. A. Bizzell, *J. Amer. Soc. Agron.*, 1916, **8**, 81.

As regards sulphur, it was found that the unlimed soil, which had received some farmyard manure, lost 49 kilos. of sulphur per hectare, and that the limed soil lost a greater amount. The soils which received potassium sulphate every year lost from one-half to one-third of the sulphur in the drainage.

Soil Acidity.

An investigation of some unsatisfactory soils near Jena showed that they were more or less acid, owing, probably, to the action of a superficial layer of raw humus in former times.[16] Some of the soils which are still covered with humus are more strongly acid, and these react with solutions of neutral salts. As a rule, the power of reacting with potassium chloride belongs chiefly to the subsoils and to the uncultivated portions, so that cultivation seems to remove the kind of acidity which, according to Daikuhara, depends on replacement of iron and aluminium by stronger bases and the hydrolysis of the resulting iron and aluminium salts. Most of the cultivated, acid surface soils reacted only with sodium and calcium acetate.

In order to throw further light on the process by which acidity is produced, other soils from pine forests were investigated. The soils were covered with layers of raw humus from 1 to 3 cm. thick; all of them reacted with potassium chloride, and when boiled with normal solutions for an hour the filtrates showed strong acidity when titrated with sodium hydroxide, and gave white precipitates consisting mainly of aluminium hydroxide. The acidity, which decreased with the depth at which the samples were taken, disappeared at a depth of 1·5 metres.

As regards the action of humus in producing soluble aluminium and iron salts in soils, it is shown that the true acidity of humus extracts is approximately the same as that of acetic acid solutions of the same strength, and that mineral soils when treated with extracts of humus render the soils capable of reacting with potassium chloride, with production of acidity. Some vegetable residues, only partly humified, produce the same result.

Incidentally, the results, if correctly interpreted, furnish conclusive evidence that humic acids are not merely adsorbing colloids, but that they are chemically acid.

Different manures affect soil acidity, due to the presence of iron and aluminium salts, in different ways, chlorides, nitrates, and sulphates increasing the acidity, whilst applications of acid phos-

[16] H. Kappen, *Landw. Versuchs-Stat.*, 1916, **88**, 13; **89**, 39; *A.*, i, 876.

phate, owing to the production of insoluble iron and aluminium compounds, diminishes the acidity.[17]

The strongest argument in favour of adsorption, and against the existence of true acids, in cases of soil acidity has perhaps been the failure to show that such soils take up chemically equivalent amounts of different bases. It is now, however, pointed out that this law only holds good when all the resulting substances are in a true solution or when the solubilities of the partly soluble compounds which may be formed are of the same order.[18] The possibility of secondary reactions has, moreover, to be eliminated. The difficulties have been overcome by employing only small amounts of finely powdered soil and large volumes of salt solutions, and the time was limited to about a minute. Under these conditions, nearly equivalent amounts of different bases are used.

Whilst some substances may be adsorbed more than others, a selective adsorption of ions from the common alkalis and alkaline earths seems to be doubtful. In any case, the amounts concerned are only small, and might be attributed to chemical reactions with impurities in the adsorbent. The acidity of cotton washed with water, which was attributed by Cameron to selective adsorption, is now thought to be due to the presence of insoluble fatty acids. The acidity observed in soils, whether active or latent, is much greater in extent, and is in every way comparable with chemical action between acids and bases, etc.

In upland soils, most of the acids causing acidity are insoluble, and the more the soil is leached with water the more acid it becomes, owing to the washing out of the bases liberated by weathering. Sodium and calcium are removed to a greater extent than potassium and magnesium. When alkali and alkaline earth bases are not present in sufficient amounts, the acid silicates may take up iron and aluminium, as is the case in acid soils.

It has been pointed out that the acidity of soils, as hitherto estimated, is the total, or potential, acidity, whilst it is probable that the effects of the acidity depend rather on the intensity of the acidity, which these methods fail to show, than on the amount of acid.[19] The intensity of acidity, or of alkalinity, has been estimated by measuring the hydrogen-ion concentration. The hydrogen-ion exponents of a number of soils which were investigated were found to vary between 4·4 and 8·6, an exponent of 7 indicating neutrality, whilst the lower and higher numbers indicate respectively acidity and alkalinity.

[17] S. D. Conner, *J. Ind. Eng. Chem.*, 1916, **8**, 35 ; *A.*, i, 359.
[18] E. Truog, *J. Physical Chem.*, 1916, **20**, 457 ; *A.*, i, 591.
[19] L. J. Gillespie, *J. Washington Acad. Sci.*, 1916, **6**, 7 ; *A.*, i, 303.

In all these experiments, soil suspensions, and not extracts, were employed. In acid soil extracts difficulties occur, owing to the slow reduction of nitrates, which, however, has no appreciable effect when suspensions of soil are employed, owing probably to the large excess of potential acidity.[20] The amount of water employed in relation to the soil seems, within wide limits, to have very little effect on the results, so that it may be assumed that the ion concentration of soil suspensions and soil solutions are approximately the same. The presence of carbon dioxide does not seem to have any appreciable effect in acid soils; in alkaline soils, on the other hand, the reaction depends largely on the equilibrium between gaseous carbon dioxide, dissolved carbon dioxide, CO_3-ion, and HCO_3-ion.

Addition of potassium, sodium, and barium chlorides to soil suspensions resulted in a distinct increase in the hydrogen-ion concentration, which, on the whole, was greater when barium chloride was used.

All the results seem to point to the presence of soluble acids as the cause of soil acidity and to make it unnecessary to suppose that physical adsorption has anything to do with it. Although there may be nothing improbable in a limited adsorption of a compound, the theory of selective ion adsorption seems, among other things, to disregard the ionic equilibrium.

Some experiments in which a number of soils were treated with *N*-solutions of potassium nitrate[21] showed that whilst calcium and magnesium were always dissolved, the more acid extracts contained aluminium as well, but no iron. The conclusion is drawn that the acidity of extracts is caused by a hydrolysed calcium salt, and that there is no excess of either acid or base unless originally present in the soil.

The Organic Matter of Soils.

An investigation in Sweden of mineral soils containing large amounts of humus showed that mechanical analyses are superfluous for the purpose of classification, and that the best indications are obtained by estimating the weight per litre and the maximum amounts of water which can be mixed with the soils without causing them to flow.[22]

The results of earlier investigations on soluble humus, carried out for many years in California, indicated that whilst arid soils contain relatively small amounts of humus as compared with humid soils, the percentage of soluble nitrogen is far higher in the former

[20] L. T. Sharp and D. R. Hoagland, *J. Agric. Research*, 1916, **7**, 123.
[21] F. E. Rice, *J. Physical Chem.*, 1916, **20**, 214; *A.*, i, 360.
[22] A Atterberg and S. Johansson, *Internat. Mitt. Bedenk.*, 1916, **6**, 38.

than in the latter, so that the total soluble nitrogen in the two types of soils tends to be equalised. To some extent this view is supported by the bacteriological results already referred to,[23] which showed that the organisms which destroy cellulose are more active in arid than in humid soils, whilst the organisms which directly affect the nitrogen content of the soils, whether by increasing or retarding losses of nitrogen, seem to be more active in humid soils. No method of estimating humus has, however, as yet been devised which can be considered quite satisfactory, and the evidence now obtained seems to show that by extracting soils with ammonia the results may be far too high, even when the extract is boiled for some hours with magnesia before estimating the nitrogen.[24] It is suggested that in soils from humid regions, the error would be diminished by the greater absorptive power of such soils for ammonia, whilst with arid soils, which are less absorbent, the error would be increased. Whatever the cause of the high results previously obtained with arid-soil humus, recent analyses, in which the humus was extracted with sodium or potassium hydroxide, did not give nitrogen percentages higher than 7 or 8 per cent., and indicate that the humus of arid soils is not more nitrogenous than that of humid soils.

The observations of Hilgard and Jaffa showed that when soils are thoroughly extracted with ammonia, no coloured substance is obtained by extracting with sodium or potassium hydroxide, and vice versa. The extracts are, however, not necessarily identical, since the one solvent may dissolve more non-coloured matters than the other.[25]

A number of estimations in which soils were extracted with 4 per cent. potassium hydroxide for nine days, which is shown to give the maximum amount of humus, gave results agreeing fairly well with those obtained by the Hilgard-Jaffa method. Five out of sixteen arid soils were found to contain humus with more than 10 per cent. of nitrogen, whilst no humid or semi-arid soils gave such high results.

The recent results, whilst somewhat conflicting, would seem, at any rate, to show that high percentages of nitrogen in arid-soil humus are not sufficiently general to enable a distinction between arid and humus soils to be made on the strength of the character of the humus as regards its nitrogen content.

The results of an investigation of Nebraska loess soils showed[26]

[23] C. B. Lipman, *loc. cit.*
[24] C. B. Lipman, *Soil Sci.*, 1916, **1**, 285.
[25] F. J. Alway and E. S. Bishop, *J. Agric. Research*, 1916, **5**, 909.
[26] F. J. Alway and M. J. Blish, *Soil Sci.*, 1916, **1**, 239.

that the amount of humus decreases from east to west, being coincident with a decrease in the rainfall from more than 750 mm. to less than 500 mm. The percentages of nitrogen in the humus from the humid and the semi-arid districts do not, however, show any marked differences. The soluble pigment in the surface soil decreases with the humus, whilst with the subsoil there was an increase from the third to the sixth foot. Comparison of the colour of subsoils was found to be difficult, owing to colouring matters other than the soluble pigment, and the colour of the subsoil and the amount of the soluble pigment have no definite relation to the total nitrogen and the soluble humus.

The soils, even in the most easterly portion of the transition region, seem to be paler in colour and shallower than the typical Russian black soils, and in the west resemble rather the brown soils which occur near the borders of the black soil zones in Russia.

With reference to the pigment,[27] it has been shown that it probably rarely exceeds 40 per cent. of the humus, and that it contains relatively low amounts of nitrogen, and is therefore of no great importance in connexion with soil fertility. It was found in all mineral soils, but not in acid peats.

Apart from the pigment, the forms of nitrogen in soil humus do not seem to differ much from those of non-humified vegetable substances, except that the latter contain large amounts of nitrogen soluble in 1 per cent. hydrochloric acid. As already suggested, ammonia and sodium hydroxide in 4 per cent. solutions extract different substances as well as different amounts from soils; it was found that the former extracts less carbon and more colour than the latter.

To the now fairly long list of definite organic compounds which have been found to be associated with soil humus, α-crotonic acid has recently been added.[28] The substance was isolated from a fine, sandy loam in Texas, which is deficient in lime and is insufficiently drained; the soil has a high reducing power and a somewhat low oxidising power, so that the conditions are favourable for the production of organic acids. The presence of this acid may be due to the hydrolysis of vinylacetonitrile (allyl cyanide) which occurs in some plants, or it might be produced from β-hydroxy-acids formed during the destruction of cellulose.

Satisfactory evidence has been obtained that the phosphorus dissolved from soils by dilute alkali is present largely in organic forms,[29] so that the view of Grandeau, who held that the phos-

[27] R. A. Gortner, *Soil Sci.*, 1916, **2**, 395,
[28] E. H. Walters and L. E. Wise, *J. Agric. Research*, 1916, **6**, 1043.
[29] R. S. Potter and T. H. Benton, *Soil Sci.*, 1916, **2**, 291.

phorus is entirely organic, is more nearly correct than that of van Bemmelen, who believed it to be absorbed inorganic phosphorus. Very little is known about the organic phosphorus compounds present in the organic materials usually applied to soils, and in addition to the nucleoprotein and other substances thus added, the production of organic phosphorus compounds from inorganic materials by bacteria may be of some importance. It was found that soils which received the more inert manures, such as peat and straw, contained less organic phosphorus, in relation to the total amount, than other soils. It will be desirable to study the behaviour of plants towards organic phosphorus compounds, very little, if anything, having been done in this direction beyond a few experiments with lecithins.

Soil Toxins.

The results of an investigation on the toxic action of decayed vegetable substances[30] showed that the products of the decay of potatoes, turnips, and *Nymphaea* rhizomes are all toxic to plants; it was also found that fresh *Nymphaea* rhizomes, when extracted with water under 33 kilos. pressure, yield a substance injurious to growing plants.

From decayed *Nymphaea* rhizomes, toxic substances were obtained by directly extracting with water. The extract retains its toxic properties when extracted with ether, and the ether extract is also toxic. When the decayed rhizomes are distilled with water at 40°, both the distillate and the residue are toxic.

The toxicity of the solutions when diluted is more or less destroyed by neutralising with sodium hydroxide, and it is removed by animal charcoal, whilst the extract, even when not diluted, is rendered harmless by precipitation with ammonium sulphate. Aeration, obtained by frequently shaking 50 c.c. of the solution in a large flask for three days, failed to diminish its toxicity.

The conclusion drawn from these results is that at least three classes of somewhat toxic substances are formed or released during the decay of many vegetable matters—colloids, very volatile substances, and certain bases. Although these products are not readily oxidised in solution, it seems probable that when formed in soils they would be more or less rapidly destroyed or otherwise rendered harmless.

Whilst the toxicity of extracts of non-productive soils can be overcome by treatment with charcoal and some other substances, it has been shown by field experiments, extending over a number of years, that addition of carbon black to the soil is without

[30] G. B. Rigg, *Bot. Gaz.*, 1916, **61**, 295.

effect.[31] A number of experiments have now been made in which porous vessels filled with carbon black were buried in the soil, so that the substances absorbed by the carbon were removed beyond the reach of the roots. For soils in pots and on greenhouse benches, ordinary battery cylinders were employed, whilst in plot experiments, drain-pipes, specially made of thin cement, were used. The results of the pot and greenhouse experiments showed that the presence of carbon black, enclosed in this manner, increased the yields of plants grown in a poor, unproductive soil and in soil to which salicylic acid and vanillin respectively had been added. In the field experiments it was shown that by burying porous tubes filled with carbon black, charcoal, and calcium carbonate in the soil, the yield of cowpeas was considerably increased, especially on the plots which had charcoal.

The amounts of substances absorbed were too small for identification. It was found, however, that all three absorbents contained a small amount of fatty acids, and that the calcium carbonate contained aldehydes as well. The latter were probably absorbed by the carbon and then oxidised.

Soil Fungi and Bacteria.

In a preliminary communication from the U.S. Bureau of Plant Industry, containing the results of an investigation of twenty-four *Azotobacter* cultures and eighteen strains of other organisms,[32] it is shown that all the bacteria studied exist alternately in an organised and in an amorphous stage, in which the contents of the separate cells become mixed through the disintegration of the cell walls. From this "symplasm" new cells are formed, which develop in different ways, according to the different formation and quality of the symplasm. Finally, cells of normal type are again produced.

The wide morphological differences obtained with *Azotobacter* occur under suitable conditions with all bacteria, and the development of the bacteria is characterised by the regular occurrence of many different forms definitely related to each other. In addition to the formation of the symplasm, it is found that the contents of the cells may interact by the direct union of two or more individual cells.

Apart from the value which, if confirmed, the results should have in connexion with systematic bacteriology, it is suggested that they afford an explanation of the regular seasonal variations in the activity of soil organisms, which may be due to the effect

[31] J. J. Skinner and J. H. Beattie, *Soil Sci.*, 1916, **2**, 93.

[32] F. Löhnis and N. R. Smith, *J. Agric. Research*, 1916, **6**, 675.

of season on the different ways of multiplication and propagation of the bacteria.

In connexion with the sterilisation of soils, it has been found that the intermittent heating of moist soil in air at 82° for five days is very effective, whilst the soluble matter of the soil is increased 46 per cent. as compared with sixteen times that amount with steam sterilisation.[33] Indications were obtained that an intermittent application of volatile antiseptics, in a partial vacuum or in conjunction with heat, for more than three days would result in complete sterilisation without any material chemical change in the soil.

A good deal of attention has been given to the fungi of soils, which have been somewhat neglected until recently, and there can be no doubt that these organisms are of considerable importance as agents in the production of food for the higher plants.

The examination of a number of soils revealed the presence of more than a hundred distinct species of fungi, belonging to thirty-one genera.[34] Indications were obtained that a distinct fungus flora exists, but this can only be established by the investigation of many soils from different localities.

Many of the fungi were found to have the power of decomposing cellulose, and their activity would seem chiefly to be exercised in the production of humus and in the liberation of ammonia from organic compounds. The greatest accumulation of ammonia was found to take place during the period preceding spore formation.[35]

Experiments in which sterilised soil was inoculated with three different fungi[36] showed that ammonification of cottonseed meal and of dried blood only takes place within comparatively narrow limits of reaction, and that it is greatest between the neutral point and an acidity corresponding with 2240 kilos. of lime per hectare; greater acidity or alkalinity, however slight, are unfavourable. From these results, it seems likely that fungi are important for ammonification when the conditions are unfavourable for bacteria.

As regards the influence of different forms or organic matter on the activity of fungi, it has been found that substances of vegetable origin are, on the whole, the most suitable.[37] The results vary, however, a good deal with closely allied groups of organisms supplied with the same organic matter. The behaviour

[33] D. A. Coleman, H. C. Lint, and N. Kopeloff, *Soil Sci.*, 1916, **1**, 259.
[34] S. A. Waksman, *ibid.*, 1916, **2**, 103.
[35] S. A. Waksman and R. C. Cook, *ibid.*, **1**, 275.
[36] N. Kopeloff, *ibid.*, 541.
[37] D. A. Coleman, *ibid.*, **2**, 1.

of the different fungi in relation to aeration and towards manures showed considerable variations.

A fungus has been found in soils, straw, and in animals which digests cellulose and readily utilises mannitol and ethyl alcohol.[38] In the latter substance it is remarkably resistant; it will grow in 80 per cent. alcohol, whilst even 96 per cent. alcohol does not destroy the spores. When a culture solution containing cellulose is filtered through a Berkefeld filter, the filtrate, free from cells, continues to dissolve cellulose for several weeks.

The group of *Actinomyces*, which form an important portion, as regards numbers, of the soil flora, has been found to occur much more abundantly in grass soils than in arable soil.[39] As active agents in the decomposition of humus, their chief importance is probably connected with the formation of humus. In the liberation of ammonia they seem to be of minor importance.[40]

In a more general investigation of the organisms which decompose cellulose, it was found that sixty-nine Californian soils all contained one or two active forms, and that most of the species were found in soils from widely separated districts.[41] Fifteen new species were isolated, in addition to seven others. The organisms assimilate the nitrogen of ammonium salts, nitrates, and organic compounds, peptone being the most suitable of these and casein the least suitable.

The importance of cellulose bacteria in soils is evident, as until the cellulose is decomposed it is useless to other organisms. On the other hand, the value of cellulose would be much less if it were at once converted into carbon dioxide and methane, which occurs under some conditions. In these experiments, no evolution of gas was observed, and it seems possible that, under natural conditions, the combined efforts of different organisms may result in the production of nitrogenous humus from cellulose and free or inorganic nitrogen.

In a promising investigation on the activities of soil bacteria in relation to the yield of crops when maize or clover was grown continuously, and in different rotations, of two to four years, indications were obtained that certain activities—ammonification and nitrification—are closely associated with crop yields.[45] Fixation of nitrogen seems to be less trustworthy as an indication of fertility, and can only be depended on in certain cases. It was

[38] W. Ellenberger, A. Scheunert, W. Grimmer, and A. Hopffe, *Zeitsch. physiol. Chem.*, 1915, **96**, 236; *A.*, 1916, i, 588.

[39] E. J. Conn, *New York Exper. Stat. Techn. Bull.*, 52, 1916.

[40] S. A. Waksman, and R. E. Curtis, *Soil Sci.*, 1916, **1**, 99.

[41] J. G. McBeth, *ibid.*, 437.

[45] P. E. Brown, *J. Agric. Research*, 1916, **5**, 855.

found, for instance, that greater crops were obtained in a three-year rotation than in a two-year rotation, and that the latter gave higher results than the continuous growth of the same crop. The bacteriological tests usually showed exactly the same relations.

The experiments, which were continued for a second and third year, showed that the plots ranked differently each year, owing chiefly to altered seasonal conditions, both as regards crop yields and, coincidently, the bacterial activity of the soils, so that, independently of season and with varying amounts of soil moisture, crop production and the activity of the bacteria remained relatively similar.

As regards the effect of farmyard manure, applications up to 16 tons per acre resulted in increased yields, whilst with 20 tons the yield was less than with 12 tons. Both ammonification and nitrification experiments agreed with the crop results, bacterial activity being increased by farmyard manure up to 16 tons and retarded by larger amounts. The crop yields and the bacterial activity, including fixation of nitrogen, were also increased by 2 tons of ground limestone; with larger amounts, the bacterial activity alone was increased.

The effects of continuous cropping and a rotation on soil bacteria has also been investigated on plots which have received the same treatment for twenty-five years.[46] It was found that, on the unmanured plots, the numbers of bacteria were greatest where timothy was grown continuously, next on the rotation plots, and least on the continuous maize and wheat plots. Addition of farmyard manure considerably increased the number of bacteria, and, at the same time, almost reversed the order of the plots, the maize and wheat plots having much the greatest numbers of bacteria, and the timothy and rotation plots the lowest. The ammonifying power of the soil seemed to have no relation to the number of bacteria and to remain practically unaltered under the different systems of cropping. The nitrifying power of the soils was found to vary considerably, the continuous growth of maize and wheat, without manure, resulting in a relatively low nitrifying power, whilst addition of farmyard manure, and, to a less extent, of chemical manures, increased the nitrifying power of the soils, especially on the plots under continuous maize and wheat.

In another series of experiments, made in pots, different amounts of farmyard manure and water were added to a calcareous soil, which was then left for four months.[47] Inoculation experiments with synthetic media then showed that the greatest number of

[46] P. L. Gainey and W. E. Gibbs, *J. Agric. Research*, 1916, **6**, 953.
[47] J. R. Greaves and E. G. Carter, *ibid.*, 889.

organisms developed when soils containing the largest amount of farmyard manure (25 tons per acre) were employed; the ammonifying and nitrifying powers of the bacteria were also highest in these soils, whilst fixation of nitrogen was most active in the case of the soils which had only 10 tons of manure.

In a fallow field soil, the bacterial numbers were found to be increased by farmyard manure up to 15 tons (the largest amount employed), and by irrigation water up to 50 cm.; ammonification was also increased by the same amount of manure and by 25 cm. of water, larger amounts of water having a depressing effect, especially in conjunction with farmyard manure. Nitrification was increased by farmyard manure and diminished by irrigation.

As compared with fallow, cropped soil showed lower bacterial numbers and lower ammonifying and nitrifying powers. In accordance with results previously referred to, a close relation was found to exist between the crop yields and the bacterial numbers and bacterial activity on soil with 5 and 15 tons respectively of farmyard manure.

Under ordinary conditions, the nitrogen–carbon ratio in soils tends to become narrower as time goes on, until only the more inert substances remain, so that when this ratio is found to be a narrow one, it is likely that the soil is deficient in fresh organic matter.[48]

Experiments in which a considerable variety of organic manures was added to a soil showed that all the common humus-forming materials were favourable to increased bacterial activity, and that the effects produced depended rather on the chemical constitution of the substances added than on their nitrogen–carbon ratios. As regards ammonification, the greatest effects were produced by horse and cow manures, rotted manure and timothy hay, whilst straw had less effect and leguminous hays least of all. Nitrification was influenced much in the same manner, except that leguminous green manures gave higher results than the non-legumes.

For fixation of nitrogen, straw and non-leguminous hays were almost as efficient as dung, whilst leguminous hays gave the lowest results. It may, accordingly, be more economical to employ non-leguminous straws, and thus increase fixation of nitrogen, than to add the more nitrogenous and more costly materials, which are less favourable to nitrogen fixation.

Manures with narrow nitrogen–carbon ratios increased the yield of oats; those with wide ratios decreased the yields, the nitrogen of the manure being of importance in the soil employed. The second crops were, however, benefited as much by non-leguminous

[48] P. E. Brown and F. E. Allison, *Soil Sci.*, 1916, **1**, 49.

as by leguminous plants, owing to increased fixation of nitrogen in the longer interval.

It has been found that addition of dried blood to a sandy loam[49] resulted in a rapid production of ammonia, which continued for eighty-six days, after which there was a marked decrease until the end of the experiment, which lasted 240 days. In the whole period, 79 per cent. of protein nitrogen was converted into ammonia, whilst of the monoamino-acids about 89 per cent. was ammonified. Arginine and histidine each gave up about 83 per cent. of their nitrogen. The soil was found to contain substances like protein, soluble in 1 per cent. sodium hydroxide; it is, however, doubtful whether these are residues from the dried blood or whether they are newly formed proteins.

The results of experiments with a large number of humid and arid soils showed that the latter do not, as Hilgard supposed, nitrify more intensely than the former.[50] Ammonium sulphate and cotton-seed meal were nitrified more vigorously in the arid soils, whilst with dried blood and with the soil nitrogen itself, nitrification was more active in the humid soils. Dried blood is ammonified very rapidly, and in soils with relatively low adsorptive power the ammonia may become strongly toxic to nitrifying organisms. The dissolved organic matter in arid soils may also have an inhibiting effect.

A number of experiments have been made on the influence of various salts on the ammonification of dried blood in a silt loam.[51] Taking first the salts of sodium, potassium, calcium, and magnesium, of which the chlorides, sulphates, nitrates, and carbonates were employed, it was found that sodium sulphate, potassium chloride and sulphate, calcium chloride and nitrate, and magnesium nitrate all failed to stimulate ammonification in any concentration, whilst all the other salts increased ammonification in some concentration.

As regards toxicity, it is shown that usually chlorides are the most injurious, then nitrates, sulphates, and carbonates, and that toxicity depends more largely on the electronegative than on the positive ions. Compounds which are toxic in the lowest concentration when different salts are compared are not necessarily the most toxic in higher concentrations, the toxicity of some salts increasing with concentration more than that of others, so that a salt which in low concentrations acts as a stimulant may, as the amount is increased, be more toxic than a corresponding

[49] E. Lathrop, *Soil Sci.*, 1916, **1**, 509; *A.*, i, 703.

[50] C. B. Lipman, P. S. Burgess, and M. A. Klein, *J. Agric. Research*, 1916, **7**, 47.

[51] J. E. Greaves, *Soil Sci.*, 1916, **2**, 443.

amount of a salt which has no stimulating action in any concentration.

Iron salts in small amounts stimulated ammonification, the greatest effect being obtained with the chloride (5·8 per million of iron), whilst with the other salts twice as much had to be added to produce the maximum stimulation, which was much less marked with the sulphate and the chloride. With increasing concentration, the toxic point was observed first with ferric sulphate, whilst in the higher concentrations the chloride was most toxic.

In the case of manganese it is shown that the sulphate, when applied at the rate of 17·2 per million of manganese, increased the production of ammonia 23·8 per cent., and that the nitrate also gave a considerable increase. The carbonate, which is usually supposed to have the greatest stimulating effect on higher plants, had much less influence on ammonification, whilst it seems doubtful whether the chloride can act at all as a stimulant.

The amounts of sodium, calcium, potassium, and magnesium which reduce ammonification to half normal have the same effect on the growth of wheat; the other salts seem to be less toxic with ammonifying organisms than with higher plants.

In another series of experiments on the ammonification of dried blood, this time in a clay loam, it was found that manganese chloride is toxic in amounts of 0·03 per cent. or more, whilst with smaller amounts ammonification was perhaps slightly stimulated.[52] Manganese sulphate had a decidedly stimulating effect when applied at the rate of 0·005 to 0·09 per cent.; with the nitrate, the results with the smallest amounts, although somewhat conflicting, seem to point to a slight stimulation. With 0·1 per cent. of manganese oxide, ammonification was distinctly retarded; larger amounts failed to produce any further decrease.

In nitrification experiments with the same clay loam, it was found that small amounts of manganese chloride have a distinctly stimulating action; the smallest amounts of sulphate stimulated nitrification, whilst a slightly increased amount, sufficient to retard ammonification, had no effect either way on nitrification, which was also retarded by the nitrate and oxide.

Applications of 0·5 to 1 per cent. of sulphur have been found to result in a great increase in the number of soil organisms; the action is slow, and no reduction in numbers was observed until after forty-four days.[53] The same amounts of sulphur increased ammonification considerably, whilst nitrification was decreased after thirty days, owing probably to the increasing acidity.

[52] P. E. Brown and G. A. Minges, *Soil Sci.*, 1916, **2**, 67.
[53] W. Pitz. *J. Agric. Research*, 1916, **5**, 771; *A.*, i, 870.

Sulphofication.

Experiments made in a loam well supplied with organic matter showed that monocalcium phosphate, acid phosphate, rock phosphate, and small amounts of calcium sulphate all increase the sulphofication of free sulphur in the soil.[54] Calcium carbonate, applied in the usual amounts to acid soils, considerably increased the oxidation of sulphur, and even very large amounts acted favourably. Magnesium carbonate increased sulphofication only when small amounts were applied.

It has been suggested that the formation of sulphuric acid from sulphur by means of soil organisms might be utilised for the production of available phosphoric acid from insoluble phosphatic manures, and a number of experiments have been made in which sulphur and rock phosphate were mixed with sand and with two different soils, all of which were inoculated with a soil infusion.[55]

The results are promising, especially those obtained with a red loam, in which 1·982 grams of soluble phosphoric acid (an increase of 1·840 grams) was produced in 100 grams of soil in fifteen weeks. In another loam the gain was less than half that amount, whilst in sand it amounted to 0·282 gram.

The production of acid in sand was greater when both sulphur and phosphate were added than with sulphur alone, and the maximum acidity was reached in the tenth week. In the red soil, with sulphur only, the acidity increased up to the end of the fifteenth week, although only slowly after the tenth week. Whilst the soluble phosphoric acid in sand showed a relatively slight increase after the tenth week, the most striking gain in the red loam was from the twelfth to the fifteenth week.

The results seem to justify the conclusion that it will be practicable to produce soluble phosphoric acid by adding insoluble mineral phosphates to compost heaps in which sulphofication is active.

Fixation of Nitrogen.

In continuation of experiments on the action of arsenic compounds on soil organisms, which showed that both ammonification and nitrification are stimulated by small amounts of these compounds, the behaviour of nitrogen-fixing organisms has now been investigated.[56]

The compounds employed in these experiments were sodium and

[54] P. E. Brown and H. W. Johnson, *Soil Sci.*, 1916, **1**, 339.
[55] J. G. Lipman, H. C. McLean, and H. C. Lint, *ibid.*, 533.
[56] J. E. Greaves, *J. Agric. Research*, 1916, **6**, 389.

lead arsenates, zinc arsenite, arsenic trisulphide, and Paris-green, and it was found that all these substances, except the last, stimulate nitrogen fixation in soils. The most active stimulant is lead arsenate, which does not become toxic until the amount of arsenic exceeds 400 per million. Zinc arsenite is the least active stimulant, whilst Paris-green was found to be very toxic, owing to the copper and not to the arsenic it contains.

The stimulating action of arsenic compounds, which is greatest when the water-soluble arsenic amounts to about 10 per cent., was observed in soils which varied considerably in chemical and physical properties.

Experiments with three types of *Azotobacter* showed that only one of them was stimulated by arsenic; with this type the increase in the amount of nitrogen fixed was considerable.

The increased fixation of nitrogen, resulting from the addition of compounds of arsenic, is attributed to the more economical utilisation of carbonaceous food, to the destruction of undesirable soil organisms, to the production of soluble phosphorus, and to a stimulating action on the cellulose organisms, resulting in a more rapid production of carbonaceous materials suitable for consumption by the nitrogen-fixing organisms.

Comparing the behaviour of ammonifying, nitrifying, and nitrogen-fixing organisms towards arsenic compounds, it is shown that 400 parts of arsenic as lead arsenate has practically the same effect on the last two, whilst the ammonifying organisms are retarded more; with arsenic trisulphide the effect on the three organisms is about the same, and with the same amount of arsenic as zinc arsenite the nitrifying and nitrogen-fixing organisms act normally, whilst the activity of ammonifying organisms is considerably depressed.

With lead arsenate and with arsenic trisulphide greater amounts are required, for maximum stimulation, by nitrogen-fixing organisms than by the others. Zinc arsenite, on the other hand, has to be supplied much more liberally to nitrifying organisms than to the other two. It must be borne in mind that in these compounds the sulphur and the zinc can act as stimulants in addition to the arsenic.

The results are of considerable interest, and make it evident that in soil culture experiments with higher plants the results, favourable or otherwise, obtained when small amounts of various substances are added to the soil may be due, not to a direct action on the plants, but to increased fertility, or infertility, due to the stimulation of some organisms and the suppression of others.

Chemistry of the Growing Plant.

An investigation of the leaves of mangolds has shown that starch is almost entirely absent from the time when the root begins to develop, and the sugars begin to migrate to it.[57] Maltose is not found at all in the leaves and stems. In the early stages of growth the leaves contain an excess of sucrose over the hexoses, whilst, later on, when the sugar is being stored in the roots, the hexoses predominate in the leaf.

In the mid-ribs and stems there is always an excess of hexoses over sucrose; and whilst the amount of hexoses varies widely during day and night, and throughout the season, the sucrose remains practically constant. A steady and rapid increase in the ratio of hexoses to sucrose was observed from leaves to mid-ribs, and so on to the bottom of the stalks.

In the leaf the proportion of sucrose closely follows the temperature curve in the day time, whilst the hexoses increase faster, so that the curve showing the ratio of hexoses to sucrose is practically parallel to the temperature curve.

The results accord with Brown and Morris's view that sucrose is the primary sugar formed. In the veins it is transformed into hexoses for the purpose of transportation; and the proportion of hexoses shows a progressive increase as the root is approached. In the root the hexoses are converted into sucrose, which remains unchanged until required for the second year's growth.

Dextrose and lævulose are found in approximately equal amounts in the leaves of mangolds, whilst the results indicated an excess of dextrose.[58] It seems probable that the two substances are really present in equal amounts, as they would be if formed by inversion, and that the divergent results are due to optically active acid amides and amino-acids.

In potato leaves sucrose is the principal sugar when the tubers begin to develop, whilst the amount of hexoses is quite small—1 per cent. or less.[59] From sunrise to 2 p.m. the amount of sucrose increases, and then falls during the rest of the day and night; the hexoses fluctuate considerably during the early part of the day, owing, perhaps, to conversion into starch, or to production from starch, the proportion of which changes very little up to 2 p.m.

As soon as the sucrose reaches its maximum, at 2 p.m., soluble starch is first detected, and it increases in quantity up to 6 p.m.; coincidently, the hexoses also increase, as a result, probably, of

[57] W. A. Davis, A. J. Daish, and G. C. Sawyer, *J. Agric. Sci.*, 1916, **7**, 255.
[58] W. A. Davis, *ibid.*, 327.
[59] W. A. Davis and G. C. Sawyer, *ibid.*, 352.

the hydrolysis of the sucrose. The starch reaches its maximum at 6 p.m., after which both the starch and the soluble starch decrease rapidly until midnight to 2 a.m., when only 0·2 per cent. remains.

In the stems the reducing sugars predominate considerably over the sucrose, owing, probably, to the inversion of the sucrose for the purpose of translocation.

The same difficulty in estimating the proportions of dextrose and lævulose, as already referred to in the case of mangolds, occurs with potatoes, so that it cannot definitely be stated whether they are present in equal amounts or not. It is possible that the stems contain an excess of dextrose, as the stems seem to contain less optically active impurities than the leaves.

The degradation of the starch is probably brought about by a mixture of enzymes, similar to takadiastase, and the series of changes is: starch, dextrins, maltose, dextrose.

It has been shown that maltase is probably always present in plants in which starch degradation occurs.[60] Germinated and ungerminated cereals contain considerable amounts, and it may be present in malt when the temperature of the kilning has been too low to destroy it; and its presence in malt would account for the production of dextrose from starch.

The maltase of plants does not act directly on starch or dextrins, and no direct cleavage of dextrose from starch ever occurs. Maltose is first formed by ordinary diastatic enzymes, and is then attacked by maltase.

Experiments with the leaves of a number of plants (*Tropaeolum*, potato, dahlia, turnip, sunflower, and mangold) showed that the crushed pulp acts on soluble starch with production of reducing sugars, chiefly dextrose with some maltose; so that it seems evident that all these leaves contain maltase.[61]

Evidence has been obtained of an indirect production in plants of starch from dextrose.[62] Maize plants were grown in water cultures, under sterile conditions, in presence of dextrose and mineral nutrients, but in absence of carbon dioxide. When the leaves were exposed to light, but not otherwise, starch was found to be present. The presence of oxygen is necessary, and the portion of the solar spectrum which has most influence is that which exerts the maximum effect in the formation of chlorophyll.

The conclusion drawn from these results is that the sugar absorbed by the roots is oxidised in the plant to carbon dioxide, and that the latter is converted into starch by the usual process.

[60] W. A. Davis, *Biochem. J.*, 1916, **10**, 31; *A.*, i, 535. Also A. J. Daish, *ibid.*, 56; *A.*, i, 535.

[61] A. J. Daish, *ibid.*, 49; *A.*, i, 535.

[62] C. Ravenna, *Atti R. Accad. Lincei*, 1916, [v], **25**, i, 649; *A.*, i. 588.

A somewhat similar experiment has been made with sugar beet which was grown on absence of carbon dioxide, but with various carbohydrates in addition to nutrients, both with and without potassium.[63]

In presence of light the plants produced proteins, both with and without the presence of potassium, when sucrose, dextrose, or lævulose were added. In absence of light, proteins were formed when nitrates were added along with the carbohydrate; the presence of a potassium salt is, however, essential under these conditions. The importance of potassium in the synthesis of proteins can only be shown in absence of light.

A similarity has been shown to exist between the absorbing power of plants for saline solutions and that of soils.[64] When the stems of certain plants were immersed successively in distilled water, a 1 per cent. solution of potassium, or ammonium chloride, and again in distilled water, the presence of calcium was readily detected in the chloride solutions, but not in the distilled water. The base, potassium or ammonium, which takes the place of the calcium originally present, can, in turn, be removed by immersing the stem in a solution of calcium chloride. Chlorides, nitrates, sulphates, and carbonates of potassium, sodium, ammonium, lithium, and magnesium all produce decalcification.

Plant Nutrition and Stimulants.

The question of the calcium–magnesium ratio, which is now twenty-five years old, continues to receive attention. A series of experiments, extending over three years, and including about three hundred pot cultures, indicated that the only thing that really matters is that sufficient amounts of both substances are present, and that the ratio, within wide limits, had no effect at all.[65] Wheat, soja-beans, lucerne, and cowpeas all grew normally in 96 per cent. of dolomite and 4 per cent. of sand, in magnesian limestone, and in sand containing 7 per cent. of magnesite. Prepared magnesium carbonate applied to a silt loam had no injurious effects up to 0·7 per cent., whilst in sand, 0·35 per cent. inhibited growth.

The percentages of calcium and magnesium in wheat straw, grown under different conditions, varied considerably, whilst the yields remained the same. Plants do not necessarily take up the two substances in the proportions in which they are applied.

Incidentally, it was found that lucerne, grown in sand ex-

[63] J. Stoklasa, *Biochem. Zeitsch.*, 1916, **73**, 107; *A.*, i, 354.
[64] H. Devaux, *Compt. rend.*, 1916, **162**, 561; *A.*, i, 457.
[65] F. A. Wyatt, *J. Agric. Research*, 1916, **6**, 589.

tracted with concentrated hydrochloric acid, was found to contain far more calcium and magnesium than the original seed contained.

At Woburn, the application of ground magnesia to a soil, so as to alter the lime–magnesia ratio from 1·6 to 1·1, increased the yield of wheat grain and straw, and the percentage of nitrogen in the grain.[66]

In pot experiments the yield of wheat, grown in a soil containing 1·06 and 1·89 per cent. respectively of lime and magnesia, was considerably increased by addition of calcium carbonate. In another soil, containing more lime than magnesia, applications of magnesia were beneficial up to the point at which the calcium and magnesium became equal.

Boric acid and borax have been shown to be toxic to wheat and barley when the soil contains only 0·0005 per cent. of boron in these forms.[67] Half of that amount of boron had, however, a slightly stimulating effect.

Another series of experiments with boron has been made in connexion with the employment of borax and colemanite as larvicides.[68] It was found that leguminous plants may be injured by 0·0011 per cent. of boron, whilst other plants were not affected by that amount. No stimulating action was observed, owing, perhaps, to the amounts used not being sufficiently small. Whilst all the plants were found to contain boron—even those grown in soil without added boron—the amounts taken up varied a good deal; there was a tendency for the boron to accumulate in different parts of the plants, except in the case of leguminous plants, in which it distributed itself more evenly.

Application of sulphur to a silt loam has been found slightly to increase the growth of red clover, without, however, influencing the formation of root-nodules.[69] In Ohio, both sulphur and hydrogen sulphide were found to increase the yield of red clover.[70] In another series of experiments, applications of sulphur, whilst sometimes beneficial, were more frequently injurious, owing, possibly, to incomplete oxidation to sulphites.[71] In a soil containing plenty of organic matter, sulphur failed to have any effect at all.[72]

Comparatively few experiments have been made with strontium. At Woburn it has been found that the chloride, supplied at the

[66] J. A. Voelcker, *J. Roy. Agric. Soc. Engl.*, 1915, **76**, 331, 351.
[67] J. A. Voelcker, *loc. cit.*, p. 347.
[68] F. C. Cook, *J. Agric. Research*, 1916, **5**, 877; *A.*, i, 302.
[69] W. Pitz, *loc. cit.*
[70] J. W. Ames and G. E. Boltz, *Ohio Agric. Exper. Stat. Bull.*, 292, 1916.
[71] E. B. Hart and W. E. Tottingham, *J. Agric. Research*, 1915, **5**, 233.
[72] T. Pfeiffer and W. Simmermacher, *Bied. Zentr.*, 1916, **45**, 18; *A.*, i, 196.

rate of 0·1 per cent. of strontium, is distinctly toxic, whilst the sulphate gave negative results.[73]

Aluminium, as chloride, has been found to be very toxic to rice seedlings, growth being inhibited by solutions stronger than $N/7500$.[74]

Lead nitrate increased the growth of a number of plants, grown in water cultures, and in field experiments both sugar beet and wheat were benefited.[75] In the case of oats the yield of grain was increased, whilst the yield of straw was diminished.

The examination of a considerable number of wheat samples, obtained from different countries, invariably showed the presence of manganese, the amount being approximately the same as that of iron.[76]

Whilst applications of manganese compounds have frequently been beneficial to crops, the number of negative results has been large, and the most recent results are far from being encouraging.

Vegetation experiments with different plants in water cultures, pot cultures, and field experiments all failed to show any increased growth with manganese, whilst iron, and even copper, acted favourably on the growth of lupines.[77]

In another series of experiments, which did show some gain under the influence of manganese sulphate, it was found that sodium sulphate had a precisely similar effect.[78]

Almost equally unsatisfactory results have been obtained in a series of experiments extending over three years.[79] Indications were obtained that under favourable conditions more nitrogen may be assimilated when manganese is applied, owing to an exchange of bases. As regards stimulation, the results are largely negative.

Manures.

Some experiments on the effect of the straw in farmyard manure showed that whilst a mixture of cow and horse manure, without straw, lost rather more than 5 per cent. of its nitrogen in four weeks, the addition of 8 per cent. of wheat straw resulted in gains of nitrogen amounting to 3·7—4·8 per cent.[80] In each case there was a great increase in the number of bacteria, especially when straw was added. *Azotobacter* was not identified; it was, how-

[73] J. A. Voelcker, *loc. cit.*, p. 344.
[74] K. Miyake, *J. Biol. Chem.*, 1916, **25**, 23; *A.*, i, 590.
[75] A. Stutzer, *J. Landw.*, 1916, **64**, 1; *A.*, i, 704.
[76] W. P. Headden, *J. Agric. Research*, 1915, **5**, 349.
[77] H. Vageler, *Landw. Versuchs-Stat.*, 1916, **88**, 159; *A.*, i, 457.
[78] G. Masoni, *Staz. sper. agrar. ital.*, 1915, **48**, 822; *A.*, i, 589.
[79] P. Ehrenberg and K. Schultze, *J. Landw.*, 1916, **64**, 37.
[80] W. E. Tottingham, *J. Biol. Chem.*, 1916, **24**, 221; *A.*, i, 460.

ever, found that the activity of the nitrogen-fixing organisms was greatest in the manure with straw.

In another series of experiments, made to ascertain the effect of different kinds of litter, it was found that all the manures, with and without litter, gained nitrogen in the first four weeks, the increase with oat straw amounting to 20 per cent.[81] From the fourth to the eighth week there was a fairly rapid loss of nitrogen. So that in the end all the manures contained less nitrogen than they did at the commencement, the loss being least in the straw-littered manure.

The amount of nitrogen as ammonia, which varied from 0·7 to 1·2 per cent. of the total, showed a tendency to increase in the second week, after which there was a fall; the proportion of ammonia was, however, never at all large. The nitrogen soluble in water, representing 41—48 per cent. of the total, decreased rapidly during the first four weeks; the total losses amounted to 70—90 per cent. of the initial amounts, and were somewhat greater in the manure mixed with pine shavings than in the others.

Important deposits of potassium salts have been discovered in Catalonia.[82] In one district the amounts of carnallite and sylvinite are estimated at 2,500,000 and 1,125,000 tons respectively.

In Central Utah, extensive deposits of high-grade alunite have been found.[83] The mineral contains about 9·5—10 per cent. of potash, which can be separated only with some difficulty. Under present conditions its exploitation should, however, prove to be practicable.

N. H. J. Miller.

Within a few hours of posting the manuscript of this Report Dr. Miller was dead. He had worked at the laboratory as usual, and no one noticed any difference in him; after posting this Report he spent the rest of the evening reading and talking with his family. Apparently all was well with him, but two hours after going to bed he had a sudden pain, and before the doctor could come he had passed away. The swiftness of the blow came as a great shock to his family and his friends. Dr. Miller never sought popularity, but he never lost the friendship of those whom he had known in early days: and he was much liked by his younger colleagues for the quiet way in which he was always willing to give up time and take trouble to help in any way he could.

E. J. R.

[81] W. E. Tottingham, *J. Ind. Eng. Chem.*, 1916, **8**, (reprint).

[82] C. Rubio and A. Marin, *Exper. Stat. Rec.*, 1916, **35**, 24; *Bol. Inst. Geol. España*, 1914, [ii], **14**, 171.

[83] W. H. Waggaman, *U.S. Dept. Agric. Bulletin*, 415, 1916.

RADIOACTIVITY.

The Heterogeneity of Chemical Elements.

In the two years 1915 and 1916 since the last Annual Report on Radioactivity much more has been done to confirm the general correctness of the new views, with regard to the nature of the chemical elements and the significance of the periodic law, described in the Report for 1913. A general description of the point of view attained may not be out of place. For these new views are far more fundamental and are far more subversive of the established conceptions of chemistry even than was the discovery of the spontaneous transmutations suffered by the radio-elements. In the first place, they give us the first real knowledge of what constitutes the difference between one element and another. In the second place, they show that important differences may exist in certain properties, notably the atomic weight and stability, of elements which are completely identical and homogeneous, judged by all the usual criteria depended on by the chemist. The analysis of matter into the so-called chemical elements is indeed only a superficial analysis, and does not imply more than the superficial identity of the atomic structure. So long as all the known methods of discrimination and identification depended on properties conferred by the surface or outer shell of the atomic structure, the analysis appeared ultimate. Even the newer *X*-ray spectra, although a degree more fundamental than the older methods, are powerless to reveal any difference whatever, but the phenomena of radioactivity, in which the inner nucleus of the atom alone is primarily concerned, has shown matter to be indefinitely more complex than the chemist had hitherto realised. It may now be taken as proved that so long as the net charge of the nucleus of the atom is the same, the element will show the definite chemical and physico-chemical character associated with one or other of the ninety-two places of the periodic table, quite independently of the nature and constitution of the nucleus. Moreover, both with regard to its ordinary light spectrum and its *X*-ray spectrum investigated by Moseley, complete identity will be

found; but the same net charge of the nucleus may result from different absolute numbers of positive and negative charges, in which case atoms with identical chemical character will show different atomic masses, the mass being primarily a function, although in all probability not a simple additive function, of the number of positive charges present. If they are radioactive, they will show also differences in the manner and the rate of their disintegration and in the manner and rates of disintegration of their respective products. Even the same net nuclear charge and the same absolute number of the two opposite kinds of charges in the nucleus may be associated with different nuclear structures, in which case the manner and rate of disintegration will reveal the difference unless the atom is completely stable. By far the greater number of the recognised chemical elements are stable, and for them the sole possible criterion for recognising this new complexity is the atomic weight and the few physical properties, such as rate of diffusion, which depend directly on it. In the radioactive sequence of elements the heterogeneity is much more easily recognised, and, of course, it was first recognised in this field by the existence of the isotopic elements, that is, of elements occupying the same place in the periodic table, completely identical in their ordinary analytical and physico-chemical behaviour. The expulsion in any order of an α-particle carrying two positive charges, and of two β-particles, each carrying one negative charge, from the nucleus, for example, leaves the net nuclear charge, and with it the whole of the chemical character, identical with what it originally was, although the atomic mass has been lowered by 4 units, by the expulsion of the α-particle. Again, when the series branches, as, for example, when some of the atoms expel first an α- and then a β-particle, whilst the others expel first a β- and then an α-particle, the net nuclear charges and also the gross nuclear charge of the two resulting products are identical, but the inner constitution of their nuclei is different, their internal energy, for example, is different, and therefore their atoms are not identical. This is a finer degree of isotopy—the chemical character, spectrum, and atomic mass all alike—but the atoms are not the same, and, if the process of change proceeds further, the difference is revealed in the manner and rate of the subsequent transformation. If the atoms, on the other hand, are stable, there is no experimental method of disclosing their differences. That is to say, with regard to the ordinary elements, heterogeneity in what has hitherto been regarded as homogeneous is to be sought for by the atomic mass, but homogeneity in this respect does not preclude the existence of differences beyond the present methods of experiment to establish, but which would be revealed as soon as artificial transmutation

became possible. The atomic weight evidence may first be dealt with.

Atomic Weight, Density, and Spectrum of Lead.

The first section of the 1914 Report dealt with the work on the atomic weight of lead from various sources, radioactive and otherwise, and it was then shown that the theoretical prediction that the atomic weight of lead derived from thorium would prove to be about one unit higher, and that for uranium about a unit lower than the international value, was being borne out. The first work to be published in this field had reference to the lead derived from Ceylon thorite—not thorianite, a totally different mixed uranium and thorium mineral often confounded with it, even by some of the workers in this field. In subsequent work, 30 kilos. of the material were hand-sorted into three grades, and from the 20 kilos. in the first grade some 80 grams of metallic lead were separated. This was cast in a vacuum into a cylinder and the density determined,[1] together with that of a similar weight of ordinary assay lead similarly purified and prepared. The values of D_4^{20} were found to be 11·3465 for the ordinary lead, in good agreement with the value found by Kahlbaum, Roth, and Siedler—11·3415 for lead distilled in a vacuum—and 11·376 for the thorite lead, which is 0·246 per cent. greater. Both samples of lead were then fractionally distilled in a vacuum, and the atomic weight of the two middle fractions was determined. The lead was dissolved in dilute nitric acid in a quartz receptacle, the nitrate evaporated to dryness, and then converted into chloride by means of a current of hydrogen chloride, the temperature being gradually raised to near the fusion point of lead chloride, and weighings taken until the weight was constant. The value so found from the ratio $Pb : PbCl_2$ was, for ordinary lead, 207·199, in good agreement with the most recent determinations—207·20[2] and 207·18.[3] The value found for thorite lead was 207·694, which is 0·238 per cent. greater. Owing to the researches being interrupted by the war, only single atomic weight determinations could be done.[4]

It will be seen that, as is to be expected on the general view that the mass and constitution of the nucleus has no effect on the outer

[1] F. Soddy, *Nature*, 1915, **94**, 615.

[2] G. P. Baxter and F. L. Grover, *J. Amer. Chem. Soc.*, 1915, **37**, 1027; *A.*, 1915, ii, 456.

[3] O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1915, **36**, 355; *A.*, 1915, ii, 635.

[4] These results were communicated in two lectures to the Royal Institution, May 15 and 18, 1915; see *Engineering*, May 28, 1915, and to Section A of the British Association, Birmingham, 1915; see *Engineering*, Oct. 1, 1915, but owing to their incomplete character have not yet been further published.

electronic system of the atom, the atomic volumes of the two specimens of lead are practically the same, the specimen from thorite being 0·246 per cent. greater in atomic weight than ordinary lead and 0·238 per cent. more dense. The atomic volume is in each case 18·26 at 20°.

An important result attained in this research was that no bismuth could be found in the whole 20 kilos. of selected mineral, which effectually disposes of the many speculations that bismuth is one of the ultimate products of radioactive change. Thallium, however, was present in easily detectable amount. The supposed α-radiation of bismuth derived from Joachimsthal pitchblende[5] has been definitely shown to be due to admixture with ionium.[6]

More extended data are now available for the case of uranium–lead. The preliminary researches of O. Hönigschmid and Mlle. Horovitz,[7] which gave the figure 206·73 for the lead from Joachimsthal pitchblende residues, were undoubtedly influenced by the lead present in the crude sulphuric acid used to treat the mineral. The final value obtained for the lead from 20 kilos. of selected purest Joachimsthal pitchblende, extracted by the use of pure reagents, was 206·405. The lead from the crystallised uranium ore, examined by Marckwald, from an old primary formation in Morogoro, German East Africa, gave the value 206·046. Almost the same value, 206·063, was obtained for the lead from bröggerite from Moos, Norway, which contains 79 per cent. of U_3O_8, 4·5 per cent. of ThO_2, and 9·5 per cent. of PbO. Ordinary lead in control experiments gave the value 207·180. The arc and spark spectra of all these specimens of lead showed absolute identity.[8]

In another and more detailed examination with a grating, of the arc spectra of ordinary lead and of lead from Joachimsthal pitchblende, complete identity was also found.[9] In the case of two of the lines, λ 3500 and λ 4100, the difference of wave-length must have been less than 0·03 Å.U., whilst a more accurate comparison of λ 4058 by a Fabry and Perot étalon showed that the difference in wave-length could not exceed 0·003 Å.U. This is against the theory of Professor Hicks that the magnitude of the atomic weight enters exactly into the series relationships of spectra.[10]

Further important results on the atomic weight of lead from

[5] *Ann. Report*, 1914, 286.

[6] L. Meitner, *Physikal. Zeitsch.*, 1915, **16**, 4; *A.*, 1915, ii, 126.

[7] *Ann. Report*, 1914, 269.

[8] O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1915, **36**, 353; *A.*, 1915, ii, 635.

[9] T. R. Merton, *Proc. Roy. Soc.*, 1915, [A], **91**, 198; *A.*, 1915, ii, 119.

[10] *Ann. Report*, 1913, 265.

various uranium minerals have been obtained at Harvard, and examination has also been made of the density.[11]

Lead from the Olary ores, S. Australia, described as Australian carnotite, and known to be derived partly from admixed galena, was found to have a density, at 20°, of 11·288 and atomic weight 206·34. That from a carefully selected specimen of Norwegian cleveite had a density, at 20°, of 11·273 and atomic weight 206·085. For ordinary lead the values 11·337 and 207·18 were found. In all cases the density is proportional to the atomic weight, and the value of the atomic volume is constant at 18·28, which is practically the same as that found for thorite lead, 18·26, although the two are not strictly comparable. Other atomic weights determined were those of the lead from American carnotite, 207·004, and from Norwegian bröggerite, 206·122.

Thus at the present time varieties of lead are known varying from 207·7 to 206·05 in atomic weight and from 11·376 to 11·273 in density, and in all cases so far examined the atomic volume is constant. The spectra of the different varieties appear to be absolutely identical, the one difference in the intensity of the unimportant line, 4760·1, noticed in the first sample of thorite lead examined not having been recorded by other observers.

Period, Atomic Weight, and Spectrum of Ionium.

Possibly the finest achievement of the period under review has been the comparison in Vienna of the atomic weight and spectrum of thorium with that of the thorium separated by von Welsbach from 30 tons of Joachimsthal pitchblende and known to contain a considerable, if indefinite, proportion of the isotope, ionium. These experiments bear out an estimate of the period of ionium recently obtained from the experiments on the growth of radium from purified uranium preparations, which have been in progress for the last thirteen years, and these results may first be given.[12] These preparations showed for the first time beyond doubt that radium was being produced from carefully purified uranium, and that the rate of production was proceeding as nearly as could be seen proportionally to the square of the lapse of time from purification, as theory demands if ionium is the only long-lived element between uranium and radium. Thus for a preparation containing 3 kilos. of uranium (element) the growth after three years from purifica-

[11] T. W. Richards and C. Wadsworth, *J. Amer. Chem. Soc.*, 1916, **38**, 221, 1658, 2613; *A.*, ii, 251, 566.

[12] Compare *Ann. Report*, 1912, 320; F. Soddy and (Miss) A. F. R. Hitchins, *Phil. Mag.*, 1915, [vi], **30**, 209; *A.*, 1915, ii, 726.

tion was 2×10^{-11} gram of radium, and after six years from purification, 8×10^{-11} gram of radium. This gives for the period of average life of ionium almost exactly 100,000 years. Any ionium initially present would make the estimate of the period too low, and it was concluded that 100,000 years might be accepted as a minimum estimate, not far from the real period. Thus there must be at least forty times as much ionium as radium by weight in uranium minerals, that is, at least 12·3 grams of ionium per 1000 kilos. of uranium. The amount of thorium and its isotope, ionium, separated by Welsbach from about 30 tons of Joachimsthal pitchblende was so small and so intensely radioactive that the question as to its atomic weight became of the utmost interest. For the atomic weight of ionium, calculated from the recent value found for uranium, 238·18,[13] by subtracting eight for the two α-particles expelled, must be 230·18, and calculated from that of radium, 226·0, by adding four for the α-particle still to be expelled is 230·0. The mean of these is 230·09, whereas the international value for the atomic weight of thorium is 232·4. The first step was a careful revision by new methods of the atomic weight of thorium by the analysis of thorium bromide,[14] analogous to the method that had been used for uranium. The operations were more difficult, but the method gave very satisfactory results, and, as in the case of uranium, a lower value than the international figure was obtained, namely, 232·12. The ionium–thorium preparation referred to, treated in an identical manner, gave the value 231·51, which is nearly 0·6 unit lower. A careful comparison of the spectra of the two preparations used in the determinations showed complete identity and complete absence of impurities, thus confirming the earlier conclusion as to the identity of the spectra of these two isotopes.[15] Ionium and thorium thus furnish the second example of two elements differing in atomic weight, but spectroscopically and chemically identical. Assuming a mean 230·06 as the true value of the atomic weight of ionium, it has been calculated that in the ionium–thorium preparation with atomic weight 231·51 there must be present 29·5 per cent. by weight of ionium and 70·5 per cent. of

[13] *Ann. Report*, 1914, 272. Further determinations have since been made of the atomic weight of the uranium separated from Morogoro pitchblende. From the Pb : U ratio, this is some 3·2 times more ancient than the Joachimsthal pitchblende and is practically a pure compound, whereas that from Joachimsthal contains most of the known elements. The result found, 238·16, agrees within the limit of error with the value 238·18 previously found for the uranium from Joachimsthal. (O. Hönigschmid and [Mlle.] S. Horovitz, *Monatsh.*, 1916, **37**, 185; *A.*, ii, 484).

[14] O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1916, **37**, 305, 335; *A.*, ii, 510.

[15] *Ann. Report*, 1912, 321.

thorium. On this assumption, the life-period of ionium was found by comparing the α-radiation from a drop of the solution evaporated over a large area with that from a similar known quantity of radium. The life-period so found was 58·1 times that of radium. This is, 145,000 years for the period of average life, or 100,000 years for the period of half change,[16] and confirms in a satisfactory manner the period estimated directly from the rate of growth of radium from pure uranium compounds.

In consequence, it may be calculated that, per 1 gram of radium (element) in Joachimsthal pitchblende, there are 58 grams of ionium and 139 grams of thorium, a total weight of thorium isotopes of 197 grams. But for the excessively minute proportion of thorium in this particular mineral, the difference in atomic weight and the identity of spectra of thorium and ionium could not have been established. It follows also that the radium which constitutes the international radium standard at Paris and the Vienna sub-standards contains so minute a proportion of the isotope, mesothorium, that the α- and γ-radiations of these standards can only be affected to the extent of a few thousandths per cent., a quantity far below the limit of accuracy of radioactive measurements.

The Definition of the Atom and the Element.

The foregoing account contains most of the important new facts having reference to the existence of isotopic elements, but a large number of résumés and theoretical papers have appeared, dealing with the new conceptions and the progress made in our knowledge of the nature of matter generally. First, however, may be mentioned a thoughtful paper on the changes in chemical nomenclature necessitated by the widening of our outlook.[17] The subject is treated historically, and the gradual evolution of the meaning attached to the terms element and atom traced from the time of Boyle. Dalton's atomic theory and Boyle's conception of elements together led to the point of view that there are as many kinds of absolutely similar atoms as elements, a view that is now no longer true. Paneth recommends retaining the idea of elements previously held and speaking of all the isotopes of one element, or of a mixture of them, still as one element. The light and *X*-ray spectra would thus still remain the distinguishing criteria of a chemical element, which would be defined as a substance that cannot be decomposed into anything simpler by any chemical process. Two elements would be denoted by the same name if, once mixed, they cannot be separated by any chemical process. Atoms, on the other hand,

[16] S. Meyer, *Monatsh.*, 1916, **37**, 347, *A.*, ii, 511.

[17] F. Paneth, *Zeitsch. physikal. Chem.*, 1916, **91**, 171; *A.*, ii, 240.

would be defined as the particles of matter, unchanged by chemical analysis, which represent the limit of chemical decomposition. Elements made up of the same kind of atoms would be defined as "pure," and those comprising different kinds of isotopic atoms as "mixed." It must be confessed, when one tries to carry out these logical rules into practice, difficulties must arise. Thus radium and mesothorium are the same element, and must have the same name, and similarly with ionium and thorium. The facts will make, it is to be feared, as much havoc among these new rules as it has already done among the old. The whole trouble arises from the fact that the words atom and element imply the idea of ultimate constituents, and we know now that our analysis of matter can never be ultimate.

Theories of Atomic Structure.

Physical Properties of Isotopes.—After the discovery of the difference of density between the different varieties of lead, the general question as to the physical and chemical properties of isotopes received theoretical attention. Lindemann[18] concluded that if the atomic volumes of isotopes were the same, their elastic constants, vapour pressure, and melting points should differ, and he predicted that the lead from thorite should melt 1·5° above the melting point of ordinary lead, a prediction which, like many others, it has not yet been found possible to test. He regards the forces of attraction and repulsion between the atoms, the interaction of which results in the solid state, as originating in the nucleus. Apparently these conclusions are opposed to those drawn by Bohr.[19] Another examination from the point of view of Bohr's theory has been made by Fajans,[20] who concludes that at absolute zero the atomic volumes of isotopes should be identical, but should differ progressively as the temperature rises, the difference amounting to less than 1/10,000th part at the ordinary temperature for the isotopes of lead. The specific heats should, however, be different, the greatest difference amounting in the case of the lead isotopes to 0·75 per cent. It is clear that the further examination of the physical properties of the isotopes of lead will prove a very searching means of testing some of the newer physico-chemical theories of the solid state.

Atom Building.—A series of papers has been published giving a

[18] F. A. Lindemann, *Nature*, 1915, **95**, 7.

[19] British Association Meeting, 1915. Discussion in Section A. See *Engineering*, Oct. 1, 1915.

[20] K. Fajans, *Arbeiten aus dem Gebeit der Physik, Math. Chemie*, 623; *A.*, ii, 406.

comprehensive survey of much of the modern work and its detailed bearing on chemical problems.[21] The possible existence of isotopes may account for some of the larger departures of the atomic weights from whole numbers, such as those of magnesium and chlorine. On the modern theory, however, that mass is wholly due to electromagnetic inertia, it is not to be expected that the mass of an atom should be the exact sum of the separate masses of its constituent sub-atoms, although the deviations on this account are probably quite small. The problem of mutual electromagnetic mass, as it is called, has also been considered by other workers.[22] Indeed, in 1910, Silberstein solved the problem rigorously for the two physically important cases, either when the electric charges are entirely separated or when one is entirely within the other. His expressions, which are contained in the reference cited, make the difference between the masses of the separate components and that of the complex a relatively simply function of the radii of the electric charges and of their distance apart. Most important information as to these atomic dimensions could be immediately obtained if the atomic weights of the various products of a disintegration series could be determined to the very high degree of accuracy required. Nicholson, with an approximate solution, has already concluded, from such data as were available for thorite lead, that the mean distance apart of the α-particles in a thorium atom is of the same order as the radius of the electron.

The mean departure from whole numbers, in terms of hydrogen as unity, of the atomic weights of the first twenty-seven elements, excluding hydrogen, is nearly a constant percentage, 0·77. For oxygen, it is exactly this, and therefore the approximation to whole numbers of the atomic weights of these elements, on the basis of oxygen as 16, is very close. The chance of this being accidental is calculated at one in fifteen million. This 0·77 per cent. is regarded as the packing effect, or loss of mass when the hydrogen nuclei are packed together to form a heavy atom. As an illustration merely, of no practical application, it is calculated that a positive and negative electron would lose 0·77 per cent. of their separate masses if caused to approach to a distance apart four hundred times the radius of the positive electron. From nickel onward no tendency to approximate to whole numbers seems to exist, for the mean

[21] W. D. Harkins and E. D. Wilson, *J. Amer. Chem. Soc.*, 1915, **37**, 1367, 1383, 1396*; 1916, **38**, 169; *A.*, 1915, ii, 543, 544, 544*; 1916, ii, 241; *Phil. Mag.*, 1915, [vi], **30**, 723, *A.*, 1915, ii, 814. The paper asterisked is a summary of modern work, especially valuable in its interpretation of Nicholson's theories.

[22] L. Silberstein, *Phil. Mag.*, 1915, [vi], **30**, 370; J. W. Nicholson, *ibid.*, 659; *Proc. Physical Soc., London*, 1915, **27**, 217; *A.*, 1915, ii, 404.

departure from integers for the thirteen best determined atomic weights between nickel and barium is 0·25 unit, as it should be on a purely chance distribution.

In common with van der Broek,[23] the helium nucleus is pictured as built up out of four hydrogen nuclei and two negative nuclear electrons. The authors regard nearly all the "packing effect" to occur in the formation of these helium nuclei, the aggregation of these into more complex atoms not producing any noticeable change of mass. Along these lines, the constituent helium nuclei being regarded as much more stable than the complexes formed out of them, is to be sought the explanation of why helium and not hydrogen is expelled in the disintegration of radio-atoms. Van der Broek suggests the further aggregation, within the complex atoms, of four helium nuclei and two nuclear negative electrons, this complex being the oxygen nucleus. He ascribes radio-activity to the disintegration of these with successive expulsion of four α- and two β-particles, a common sequence in the radioactive series. This represents a change of 16 units of atomic mass for 6 of atomic number, and this, he points out, is the average for all the elements between magnesium and thorium, which differ by 208 units of mass and 78 units of atomic number, that is, as 16 is to 6.

Periodic Law.—The fifth paper of the series deals with the periodic law and its representation by helical models. Many useful data, relative especially to the physical properties of the elements, are here collected together. The authors are alive to the essential changes of outlook effected by the recent advances on the representation of the Periodic Law, but their model offers little of novelty or advantage over earlier efforts, although discussed in much greater detail. In one important point they seem to be at fault. They divide the Periodic Table into three cycles of 4^2, 6^2, and 8^2 elements, and each cycle into two periods each of 8, 18, 32 elements respectively, the last part of the last very long period of 32 elements being missing, and they argue that this represents a numerical expression of some function appertaining to atomic structure; but the series from the emanation to uranium runs like that from krypton to molybdenum, and not like that from xenon to tungsten, wherein the rare earths are interpolated.[24] Although the last very long period is incomplete, it runs far enough to make this division of the table into cycles of 4^2, 6^2, 8^2 elements fanciful. Again, the eighth group is still only accommodated in their model

[23] A. van der Broek, *Physikal. Zeitsch.*, 1916, **17**, 260; *Nature*, 1916, **97**, 479; *A.*, ii, 465.

[24] Soddy, "Chemistry of the Radio-Elements," Part II, p. 11, 1914.

on the old supposition that "a catastrophe of some sort seems to take place here," whereas these elements with their gradual change of properties are as significant and marked a feature of the Periodic Law as is the intensely abrupt change of properties that occurs on either side of the zero group.

Stellar Elements.—Fraunhofer's discovery of the dark lines of the solar spectrum, the discovery of helium, and the theory of the evolution of the heavy elements from the lighter ones that has been advanced by Lockyer as a consequence of the study of the life-history of the stars, have made chemists familiar with the fruitful bearing of astronomical observations on their own science. From such sources, aided by mathematical reasoning applied to a new theory of atomic structure, Nicholson has formed some tentative conclusions of great interest to chemists.[25]

He regards the terrestrial elements as differing in character and atomic structure from the elements coronium, nebulium, and others, the existence of which, like that of helium, has been inferred from unidentified lines in the solar corona and in nebulæ. These lines appear to him to originate from earlier and simpler evolutionary forms of matter from which the terrestrial elements have developed. It is significant that there seems to be no room in the Periodic Table, as we now understand it, for any of these stellar elements. Nicholson's model atom is of the Rutherford type, in which the electrons revolve in orbits round a central positive nucleus, but in his calculations, unlike Bohr, he does not depart from the classical mechanics or introduce the quantum hypothesis. The energy of the spectrum is not derived from internal atomic energy, but from external sources, and on this point there can scarcely be any reasonable doubt that he is correct. In spite of its great initial successes in calculating correctly the magnitude of the Rydberg constant, and in correctly ascribing the Pickering series of lines to helium rather than to hydrogen, Bohr's theory does not seem to have been generally so successful. In the Nicholson atom, the vibrations from which the spectral lines originate are perpendicular to the plane of the ring of revolving electrons. The strongest and first class of vibrations are due to the entire ring vibrating as a whole, keeping parallel to its position when not in vibration. In the second class of vibrations, the ring vibrates in halves, that is, there are two nodes and two crests travelling round the ring. In general, there are as many classes of vibrations possible as there are electrons in the ring, although

[25] Nicholson's earlier theories were fully discussed in the Annual Report for 1911, 269. The present account is derived mainly from the third paper in the series referred to, by Harkins and Wilson.

the higher classes are probably too feeble to detect. For the nebulium atom Nicholson postulates a nucleus of four positive charges. The chief line attributed to this element is $\lambda=5006{\cdot}9$, and if this constitutes what has been termed the first class, the calculated wave-length of the second class should be 4367·0, which corresponds with the strong observed line $\lambda=4363{\cdot}4$. The next should be 4352·9, and it was only after its wave-length had been calculated that a line 4352·3 was photographed at the Lick Observatory. A search of older photographs showed its existence on plates taken several years before, but it had escaped observation owing to its feebleness. Again, two lines formerly attributed to nebulium could not be obtained from the structure of the atom postulated, and these, simultaneously with this result, were shown by Wolf, of Heidelberg, to originate in a different part of the nebula from the rest.

Similarly for model atoms of 2, 3, 5, and 6 charges, by assuming one line to be due to the first class of vibration, the wave-lengths of the other classes of vibrations have been calculated and correspondence found with observed lines. Thus twenty-one out of the twenty-seven lines of the solar corona have been accounted for by the vibrations of a model atom of five charges. The atomic weights of these stellar elements can only be very indirectly and unsatisfactorily inferred, but the values given are 0·082 multiplied by the square of the nuclear charge. Thus protohydrogen is 0·082, nebulium 1·3, protofluorine or coronium 2·1.

This work thus suggests the existence of types of matter altogether unknown upon the earth, and for which no place exists in the Periodic Table. The difference between the two kinds is probably to be sought in the constitution of the nucleus of the atom. We know from the expulsion of β-particles and the existence of isotopes that negative electrons do form an integral part of the nucleus of the radioactive atoms, and that the nuclear charge or atomic number is the difference between the number of positive and negative electrons. Nicholson's idea seems to be that this is true of all terrestrial elements, including hydrogen, and that it constitutes the difference between these elements and the stellar elements. On this view, then, the hydrogen nucleus is not a single positive electron, but a combination of several with a number of negative electrons one less. This in turn involves a simpler ultimate unit of atomic structure than hydrogen, but is not necessarily inconsistent with the conception of nuclei, of helium, and of hydrogen as penultimate nuclear constituents of the more complex atoms known on the earth.

Cause of Atomic Disintegration.—For the first time, an attempt

has been made to frame a theory of the process resulting in atomic disintegration.[26] Hitherto the barrier has been the exponential law of change, which is the law of pure chance, that out of a definite number, Q, of atoms a definite fraction, λQ, break up in the unit of time, independent of every consideration whatever. On this theory, the cause of instability is that N separate particles in the atomic nucleus should all pass some critical position in the short time τ, τ being the time taken for a strain (regarded as a sound-wave) to traverse the nucleus. An analogy is given which helps to make the theory intelligible. A number of small impulses applied to a pendulum will result in a maximum displacement if all are applied while the pendulum is moving in one direction. The constant λ, then, appears as the probability of N particles being all in the critical region in the short interval τ. This is $(\tau\nu)^N$, where ν is the frequency or number of times the particle passes the critical region per second. It is shown that N is 1·5 B, where B is the constant of the Geiger-Nuttall relation between λ and the range R of the α-particle expelled, namely, $\log\lambda = A + B\log R$. N is equal to 80, which, as the atomic number is between 80 and 90, indicates that nearly all the free positive particles in the nucleus must conspire to effect its disintegration. The radius of the nucleus, evaluated on this theory from the constant A, agrees with that found by Rutherford for the gold nucleus.

High-frequency Spectra of the Elements.

As previously pointed out,[27] the discovery of the regular reflection of X-rays from crystal surfaces has been the experimental means of two distinct advances, the elucidation of crystalline structure and the determination of the wave-length of the X-rays, the latter only falling within the province of this Report. It was by this means, some six months after the elucidation of the nature of α- and β-changes had proved that the consecutive places at the end of the Periodic Table correspond with unit difference of atomic charge, that Moseley was able to extend the conception towards the beginning of the table as far as aluminium, and to call the roll of the elements, which confirmed in so striking a manner the accumulated labours of chemists since the time of Robert Boyle. Numerous extensions and confirmations of this fundamental work fall to be recorded.

In a long series of papers,[28] the L-series of spectra, for which

[26] F. A. Lindemann, *Phil. Mag.*, 1915, [vi], **30**, 560; *A.*, 1915, ii, 720. Compare also A. Debierne, *Ann. Physique*, 1916, [ix], **4**, 323; *A.*, ii, 168.

[27] *Ann. Report*, 1913, 273.

[28] M. Siegbahn and E. Friman, *Physikal. Zeitsch.*, 1916, **17**, 17; *Phil. Mag.*,

Moseley observed five line groups and measured three,[29] has been much extended. Fourteen groups of lines are now recognised in the *L*-series, and the elements examined have been extended as far as zinc in one direction to uranium in the other.[30] Indeed, very few of the elements now have not had their atomic number directly determined by measurement of the frequency of one or more of the lines in one or more of the various series. An improved vacuum spectrograph has enabled the *L*-series to be followed down to wave-length 12·35 Å., whereas the greatest wave-length hitherto measured was 8·4 Å. Only for three lines (α_1, α_2, and β_2) is the linear relation between atomic number and square root of the oscillation frequency exact. For the others the curves are slightly convex to the atomic number axis. The atomic number of uranium, the last element, is, as previously presumed, 92, thorium being 90, bismuth 83, lead 82, thallium 81, mercury 80, and gold 79, while it is claimed that the values 84 and 88 for polonium and radium have been experimentally established. With regard to lead, an interesting table is given[31] comparing twelve lines of its *L*-series spectrum with fifteen lines of the soft γ-ray spectrum of its isotope, radium-*B*, as given by Rutherford and Andrade.[32] Ten of the lines are nearly identical in wave-length, thus confirming still further the identity of the *X*-ray spectra of isotopes. Tellurium and iodine have the atomic numbers 52 and 53 respectively, as the periodic law requires. In the *K*-series, four lines have been measured for the elements chromium to germanium, and, in the most recent work, investigation has been pushed as far as sodium, with results in full accord with Moseley's work. Lastly, a new series, the *M*-series, comprising six or seven rays, softer than the *L*-series, but very similar in character to this and to the *K*-series, has been found, and the wave-length measured for the elements uranium to gold. This series also obeys the linear relation over the range studied. Thus the *X*-ray spectra are losing their pristine simplicity, but the theoretical interpretation of the various series should still be child's play to the mathematician in comparison with that of light spectra. The atomic numbers of the rare earths do not differ from those previously given.[33] Numbers 61 and 72 are still vacant, but the

1916, [vi], **31**, 403; *A.*, ii, 167; *Physikal. Zeitsch.*, 1916, **17**, 48, 61; *A.*, ii, 205, 277; M. Siegbahn and W. Stenström, *ibid.*, 1916, **17**, 318; *A.*, ii, 509; M.Siegbahn, *Ber. Deut. physikal. Ges.*, 1916, **18**, 39, 150, 278; *A.*, ii, 462, 462, 463; also *Ann. Physik.*, 1916, [iv], **49**, 611, 616; *A.*, ii, 362; *Phil. Mag.*, 1916, [vi], **32**, 39; *A.*, ii, 405.

[29] *Ann. Report*, 1914, 278.

[30] E. Friman, *Phil. Mag.*, 1916, [vi], **32**, 497; *A.*, ii, 589.

[31] *Phil. Mag.*, 1916, [vi], **32**, 49.

[32] *Ann. Report*, 1914, 275.

[33] *Ibid.*, 280.

others have all been measured except No. 69, ascribed to thulium. Urbain[34] states that celtium has not yet been discovered by this method, that there is only one thulium, one erbium, and two ytterbiums—neoytterbium and lutecium. It is to be hoped that agreement will now be reached as to the names of these elements, as several of them, having been discovered independently, have aliases. A number of other papers on this subject have also appeared.[35]

The rays from the Coolidge *X*-ray tube with a tungsten anti-cathode have been subjected to an interesting examination to determine the maximum frequency of the *X*-rays emitted under different constant voltages.[36] The hope previously expressed,[37] that this tube would enable *X*-rays as penetrating as the γ-rays of radium to be artificially generated, has now been definitely dispelled. The penetrating power and frequency of the *X*-rays reaches a maximum at 143,000 volts, and does not sensibly increase beyond this when the voltage is raised to 170,000 volts. The minimum value of the absorption coefficient, $\mu(\text{cm.})^{-1}$, Al, is 0·39, as compared with 0·115 for the penetrating γ-rays of radium-*C*. For lead the value is 23, as compared with 0·5 for radium-*C*, and 3 mm. of lead afford practically complete protection against the most penetrating *X*-rays that the Coolidge tube can produce. The limiting frequency is probably determined by the highest frequency that exists in the atom, in this case, of tungsten. It is anticipated that by the use of a uranium anti-cathode, a limiting penetrating power of $\mu=0{\cdot}23$, instead of 0·39, in aluminium could be attained. Planck's quantum theory appears to hold for the relations between frequency, ν, and voltage, E, for small voltages, but for higher voltages, instead of $h\nu=E$, the relation assumes the form $h\nu=E-cE^2$, where c is a constant. This formula does not hold beyond the maximum frequency given by $E=1/(2c)$. The voltage required to excite the most penetrating radiation is about twice what is to be expected on the quantum theory, and the efficiency at high voltage is only about 1/500th. If one-half of the energy of each contributing electron appears as radiation, this indicates that only one in some two hundred electrons contribute to the radiation. In this work there was no evidence that the radiation from the tube could be analysed into definite characteristic radia-

[34] Obituary notice of H. G. J. Moseley, *Proc. Roy. Soc.*, 1916, [A], **93**, xxvii.

[35] I. Malmar, *Phil. Mag.*, 1914, [vi], **28**, 787; *A.*, 1915, ii, 2; M. de Broglie, *Compt. rend.*, 1916, **163**, 87; *A.*, ii, 509; J. Barnes, *Phil. Mag.*, 1916, [vi], **30**, 368; *A.*, 1915, ii, 658.

[36] Sir E. Rutherford, J. Barnes, and H. Richardson, *ibid.*, 339, 361.

[37] *Ann. Report*, 1914, 277.

tions, although the initial potential, 10,300 volts, at which X-rays began to be generated corresponds well with that required to excite the L-characteristic of tungsten, and the most penetrating rays correspond with the shortest wave-length component of its K-characteristic radiation. On the other hand, de Broglie has found it possible with a Coolidge tube to follow the absorption band of an element at least as far as bismuth, and considers that his results put beyond doubt the presence of radiation far more penetrating than the K-radiation of its tungsten anti-cathode.

α-, β-, *and* γ-*Radiations.*

α-*Rays.*—Hitherto, the fastest known α-rays have been those of thorium-C', with a range of 8·16 cm. in air at $N.T.P.$ A small number of bright scintillations, undoubtedly due to α-rays, from a strong preparation of the active deposit of thorium, were observed on a zinc sulphide screen after the passage of the α-rays through the equivalent of 10·7 cm. of air at $N.T.P.$[39] Further investigations disclosed that two new sets of α-rays were probably present, one-third of range 9·7 cm. and two-thirds of range 10·7 cm. in air at $N.T.P.$ The division is just the same as for the ordinary α-rays of thorium-C, which gives two sets of different range, one-third with range 4·55 and two-thirds with range 8·16 cm. These new α-rays certainly come from the active deposit of thorium, for they decay at the same rate as the other α-rays, but it is not yet definitely proved that they come from thorium-C. It is suggested that the α-particles of 9·7 cm. range accompany those of 4·55 cm. range, and those of 10·7 cm. range accompany those of 8·16 cm. range. For each α-particle in the two new sets, 10,000 in the two old sets are emitted. The Geiger-Nuttall relation indicates that the period of average life of the atoms yielding these two new sets of α-rays must be 10^{-13} and 10^{-16} second respectively, and their velocities are estimated to be 2·18 and 2·26 ($\times 10^9$ cm. per sec.). A new determination of the velocities of the other two sets of α-rays from thorium-C gave 1·714 and 2·060 ($\times 10^9$ cm. per sec.), and this indicates that the range of the slower α-particle should be about 4·70 cm. instead of 4·55 at $N.T.P.$[40] A determination of the velocity of the α-particle from radium-A gave 1·69 ($\times 10^9$ cm. per sec.), in good agreement with that calculated from the range.[41] It has now been definitely shown[42] that the emission of δ-rays from

[39] Sir E. Rutherford and A. B. Wood, *Phil. Mag.*, 1916, [vi], **31**, 379; *A.*, ii, 282.

[40] A. B. Wood, *ibid.*, 1915, [vi], **30**, 702; *A.*, 1915, ii, 814.

[41] N. Tunstall and W. Makower, *ibid.*, **29**, 259; *A.*, 1915, ii, 80.

[42] J. McLennan and C. G. Found, *ibid.*, **30**, 491; *A.*, 1915, ii, 712. Compare *Ann. Report*, 1912, 301.

metals bombarded with α-rays is, like the photoelectric effect, dependent on a surface gas film, and in the complete absence of this no emission occurs.

Several microphotographic investigations of the tracks of α-particles in photographic films have been made,[43] and the hope is expressed that with a suitable plate (Wratten and Wainwright's lantern plate being alone found suitable) all the phenomena hitherto studied by the scintillation method can be more conveniently studied by this means. Certainly such a method would have many advantages. The halos obtained when an active needle point is made to touch a photographic plate have under the microscope many of the characteristics of the pleochroic halos. The method has been used to investigate the straggling of α-particles towards the end of the range, with results much closer in accord with a theoretical formula, calculated by Bohr, than earlier measurements by other methods.

H-Particles.[44]—This subject is in rather a confused state. Two attempts have been made, by Wilson's method, to photograph the tracks of the *H*-particles known to be produced in the passage of α-rays through hydrogen. The first[45] was not attended with success. In a large number of beautiful photographs of α-ray tracks in hydrogen, no evidence whatever of the production of *H*-particles was obtained. In the second,[46] the separation of the path of the α-particle, at the point of its collision with the hydrogen nucleus, into two distinct paths, corresponding with the recoiling *H*-particle and the deflected α-particle respectively, was clearly shown, and the number observed were in satisfactory agreement with the Rutherford-Darwin formula.

On the other hand, Marsden,[47] who first observed these *H*-particles, in attempting a quantitative verification, by counting the scintillations they produce, in an apparatus similar to that used to study the scattering of α-particles, observed effects several times greater than the formula leads to. It was then found that the α-ray tube and emanation alone were emitting *H*-particles, without any layer of paraffin-wax, which was put on as a convenient form of hydrogen atoms. The source of these is doubtful, as it seems unlikely that there was sufficient hydrogen in the glass tube, or any

[43] S. Kinoshita and H. Ikeuti, *Phil. Mag.*, 1915, [vi], **29**, 420; R. R. Sahni, *ibid.*, 836; H. Ikeuti, *ibid.*, **32**, 129; W. Makower, *ibid.*, 222.

[44] *Ann. Report*, 1914, 274.

[45] J. C. McLennan and H. V. Mercer, *Phil. Mag.*, 1915, [vi], **30**, 676.

[46] D. Bose, *Physikal. Zeitsch.*, 1916, **17**, 388; *A.*, ii, 547. Unfortunately, the abstract only is available to the writer, who has not seen the actual photographs.

[47] E. Marsden and W. C. Lantsberry, *Phil. Mag.*, 1915, [vi], **30**, 240.

condensed water film present, to produce them, and the suspicion is created that they are emitted by the radioactive atoms themselves. This seems to contradict the results of the special research made for radiant particles, differing either in mass or charge from the α-particles, in the rays from the radium emanation,[48] but in the latter it is stated that the number is certainly less than 1 in 10,000 α-particles, and possibly the two statements are not inconsistent.

β-Rays.—Two sets of β-rays, of velocity 0·51 and 0·47 times that of light, hitherto attributed to thorium-*X*, have been shown to be due to radio-thorium, which in this respect is now analogous to radio-actinium.[49] The paper contains useful information on the deposition of films of thorium-*X* and radio-thorium on short, fine wires. The two sets of β-rays emitted by radium-*D*, velocities 0·39 and 0·37,[50] have been the subject of an interesting examination. Hitherto, on account of their feeble penetrating power, which is less than that of the α-rays, they have only been detected photographically by means of their magnetic spectrum. After an extremely careful purification from radium-*E*, which gives penetrating β-rays, and radium-*F*, which gives α-rays, radium-*D* was found to be giving β-rays capable of detection by the electroscope, which were reduced in intensity to 10 per cent. of the initial value by 0·0035 mm. of aluminium. The absorption-coefficient is 5500 $(\text{cm.})^{-1}$ Al, which agrees almost exactly with the value, 5067, for cathode rays of 36 per cent. light velocity, as measured by Becker. The experiments favoured the view that the absorption of β-rays is primarily due to the complete stoppage of the individual particles in single encounters with atoms, rather than to the gradual wearing down of the velocity of the whole beam, alternatives that have previously been fully discussed.[51] With regard to the absorption of homogeneous β-rays in aluminium, the absorption curve is nearly linear and the rays have a definite "range," varying from 0·025 cm. for rays of $H\rho = 1930$, velocity 0·75, to 0·5 cm. for rays of $H\rho = 11{,}500$, velocity 0·99 times that of light. This is due to the chance balancing of the scattering and the diminution of velocity, for in paper, where the scattering is smaller, the absorption curve is concave, and in platinum, where it is large, convex to the origin.[52]

γ-Rays.—Experiments on the excitation of γ-rays by β-rays in plates of iron, nickel, copper, and zinc showed that the γ-rays excited were similar in absorption-coefficient to Barkla's character-

[48] *Ann. Report*, 1914, 274.

[49] O. Baeyer, O. Hahn, and L. Meitner, *Physikal. Zeitsch.*, 1915, **16**, 6; *A.*, 1915, ii, 127.

[50] *Ann. Report*, 1911, 278; L. Meitner, *ibid.*, 272; *A.*, 1915, ii, 663.

[51] *Ann. Report*, 1907, 315.

[52] R. W. Varder, *Phil. Mag.*, 1915, [vi], **29**, 725; *A.*, 1915, ii, 401.

istic secondary X-radiations from these metals, and, in silver and tin, with Barkla's K-radiations of these metals.[53] The absorption of the γ-rays of radium-B and -C in lead shows no such anomaly, due to the atomic numbers of these elements and of lead being similar, as might have been expected from Barkla's work on the absorption of X-rays. Eighty-five per cent. of the ionisation due to radium-C is from the well-known penetrating rays, $\mu = 0{\cdot}5$ (cm.)$^{-1}$, Pb, and 15 per cent. to rays of apparently exactly the same character as the γ-rays of radium-B. The latter comprises three types, with μ in lead, 1·5, 6·0, and 46 respectively contributing 12, 26, and 46 per cent. of the total ionisation.[54]

Radioactive Recoil.

Once the charge carried by the α-particle was a debated problem.[55] Was it intrinsic, or was it simply the result of its encounter with the first atom in its way? It was very certain that an atom travelling at such a speed would be ionised itself, even if initially uncharged. After many researches, it was finally decided that, so far as experimental tests could show, the charge was intrinsic, and now we know that it is the loss of these two charges from the nucleus in an α-ray change which is the cause of the shift of two places in the Periodic Table. Exactly the same question has now been asked of the recoiling particle,[56] which ordinarily carries a single positive charge,[57] and here also the theoretical importance of the question is considerable.[58] The recoil of radium-D from radium-C was chosen, and here it was at once found that in a sufficiently good vacuum the recoiling particle is uncharged. It gains its charge by collisions with the molecules of the gas in its path. In a vacuum at a pressure measured by the Knudsen absolute manometer to be 0·6 dyne per cm.^{2} ($4{\cdot}5 \times 10^{-4}$ mm. of mercury)—six hundred times, it may be remarked, that measured by the McLeod gauge—no charge was carried by the recoiling atoms. As the pressure rose, the charge acquired increased and, at sufficiently high pressure, equalled that carried by the α-particles, showing that the radium-D atom can acquire multivalent charges. Since at atmospheric pressure a univalent charge is carried, it is clear that, as in the case of the canal-rays, successive recombinations and

[53] (Miss) J. Szmidt, *Phil. Mag.*, 1915, [vi], **30**, 220; *A.*, 1915, ii, 721.
[54] H. Richardson, *Proc. Roy. Soc.*, 1915, [A], **91**, 396; *A.*, 1915, ii, 401.
[55] *Ann. Report*, 1904, 256; 1905, 302; 1906, 344; 1907, 315.
[56] L. Wertenstein, *Compt. rend.*, 1915, **161**, 696; *A.*, ii, 69.
[57] *Ann. Report*, 1910, 272; H. P. Walmsley and W. Makower, *Phil. Mag.*, 1915, [vi], **29**, 253.
[58] *Ann. Report*, 1913, 281.

ionisations occur along the path. It would not be safe to generalise from the case of radium-*D*, for it is produced in the excessively quick change of radium-*C'*, which itself, at the moment of its disruption, may still carry a positive charge acquired at its birth, 10^{-11} second earlier, by the expulsion of a β-ray from radium-*C*. This might lead to the expectation that in other cases the recoil-atom will be found negatively charged. The research opens out a whole series of questions as to the conservation of electric charges during radio-active changes, and further results will be awaited with interest.

Attempts have been made to detect a photographic action both of radium-*G* recoiling from polonium,[59] and of radium-*D* from radium-*C*,[60] using Schumann plates in which the amount of gelatin in the film was reduced to a minimum. No photographic and no phosphorescent effect on zinc sulphide could be detected in the first case, but, in the second, a weak photographic effect, attributed to the recoil atoms, was obtained. A line in the magnetic deflection experiment was found nearly midway between that due to the deflected and undeflected α-particles of radium-*C*, and it was concluded that the atoms of radium-*D* are projected with a single positive charge, as is the case with radium-*B* recoiling from radium-*A*. The experiments were done in a vacuum, but it is clear, from Wertenstein's results, already noted, that the charge carried by the recoiling atom of radium-*D* varies with the pressure of the gas.

A method of determining the ratio of the "ranges" of the recoiling atoms of radium-*B* and -*D* respectively from the efficiency of the recoil of the latter from a plate on which radium-*A* had been deposited indicated a greater difference in their ranges than in those of the corresponding α-particles of radium-*A* and radium-*C* respectively which accompany these recoiling atoms.[61]

Chemical Actions of the Radiations.—The spontaneous reaction between hydrogen arsenide and oxygen is accelerated by β- and γ-rays, and, instead of the arsenic being liberated as such, it is oxidised to arsenious acid, $2AsH_3 + 3O_2 = 2H_3AsO_3$.[62] The velocity of the esterification of acetic acid is scarcely increased by the action of the radium rays, but ethyl acetate is decomposed by the penetrating rays, primarily with the formation of an acid and an unsaturated hydrocarbon. The oxidation of acetone to acetic acid by

[59] A. B. Wood and A. I. Steven, *Proc. Physical Soc., London*, 1915, **27**, 189; *A.*, 1915, ii, 403.

[60] A. B. Wood and W. Makower, *Phil. Mag.*, 1915, [vi], **30**, 811; *A.*, ii, 6.

[61] W. Makower, *ibid.*, 1916, [vi], **32**, 226; *A.*, ii, 547.

[62] H. Reckleben and G. Lockemann, *Zeitsch. anorg. Chem.*, 1915, **92**, 145; *A.*, ii, 209.

radium rays is detectable, but, as is usually the case, is very slight compared with similar action brought about by ultra-violet light.[63] An investigation of the union of hydrogen and chlorine, under the influence of α-particles from radium emanation, showed that the reaction is of the first order, is not affected by the hydrogen chloride formed, and is retarded by oxygen at all stages proportionally to the oxygen concentration. As regards the kinetics of the combination, the reaction showed complete parallelism to the photochemical reaction.[64]

In a series of experiments on colloidal solutions, the penetrating rays of radium were found to precipitate electropositive, but not electronegative, colloids. Native, well dialysed albumin is changed and finally coagulated by the rays, which produce also a lowering of the coagulation temperature and increased precipitability by alcohol. Salts exercise a protective action.[65]

New Work on the Radioelements.

A number of more extended accounts of collected investigations, previously published in brief, have appeared dealing with (1) the radio-active decomposition of water; (2) the production of helium from radio-active substances; (3) the atomic weight of the radio-active emanations; and (4) the deposition of the active deposit of radium.[66]

Thorium.—The life-period of thorium has been determined as $1{\cdot}77 \times 10^{10}$ years for the period of half-change, $2{\cdot}56 \times 10^{10}$ years for the period of average life, from the ionisation of films of thorium oxide of vanishing thickness.[67]

Radium.—The life of radium has been redetermined by Boltwood's method,[68] by separating the whole of the ionium in a uranium mineral and determining the rate of growth of radium from it in terms of the equilibrium amount present in the mineral.[69] Carefully selected specimens of uraninite (N. Carolina), cleveite (Norway), and bröggerite (Norway) were used. The ionium was separated by addition and separation of thorium, several separations being carried out, and the last kept distinct for a blank test, to

[63] A. Kailan, *Monatsh.*, 1914, **35**, 859; *A.*, 1915, ii, 663.

[64] H. S. Taylor, *J. Amer. Chem. Soc.*, 1915, **37**, 24; *A.*, 1915, ii, 80.

[65] A. Fernau and W. Pauli, *Biochem. Zeitsch.*, 1915, **70**, 426; *A.*, 1915, i, 722.

[66] A. Debierne (1) *Ann. physique*, 1914, [ix], **2**, 97; *A.*, 1915, ii, 126; (2) *ibid.*, 425, 478; *A.*, 1915, ii, 132, 725, 726; (3) *ibid.*, 1915, [ix], **3**, 18, 62; *A.*, 1915, ii, 302, 303; (4) *ibid.*, 1915, [ix], **4**, 408; *A.*, 1915, ii, 667.

[67] B. Heimann, *Monatsh.*, 1914, **35**, 1533; *A.*, 1915, ii, 665.

[68] *Ann. Report*, 1909, 263.

[69] (Mlle.) E. Gleditsch, *Amer. J. Sci.*, 1916, [iv], **41**, 112; *A.*, ii, 168.

make sure all ionium had been removed. The two most satisfactory experiments gave the period of half-change as 1660 years, in good agreement with Rutherford's value, 1690 years, obtained by counting the α-particles expelled per second from a known weight of radium. The value for the period of average life is 2347 years, somewhat less than the value, 2500 years, usually taken.

Polonium.—Some indirect evidence has been obtained of the existence of a volatile hydride of polonium, in the course of experiments on the range of the α-particles in hydrogen, in which a gradual increase in the ionisation current at a given distance with the lapse of time was observed.[70] Being in the sixth family of elements, it is to be expected that it should form a volatile compound with hydrogen dissociating at the ordinary temperature.

The Emanations.—A lengthy series of experiments has been carried out on the volatility of the thorium and radium emanations to see if these two isotopes, once mixed, could be separated by condensation at low temperature.[71] A large number of puzzling phenomena were encountered, and the results obtained varied widely from experiment to experiment. Owing to this, and the great difference in the periods of average life, and, consequently, in the concentration of the two emanations, no definite conclusions could be reached on the main question, which remains unanswered. In the course of the investigation, two maxima were observed in certain cases in the condensation curve of radium emanation, one at −75° and the other at −161°. This may be connected with the well-known phenomenon that, when a tube containing emanation is immersed in liquid air, the condensation, as shown by the luminous ring on the tube, occurs always a short distance above the level of the surface of the liquid air.

The Branching Point of the Thorium Series.[72]—The supposed separation of the two sets of thorium-*C* atoms, which give α-rays of range 5·7 and 8·16 cm. respectively, has not been confirmed. The two stages in the volatilisation, 35 per cent. being volatilised below and 65 per cent. above 900°, has been confirmed, but it has been shown that the isotope radium-*C* shows in every respect a completely identical behaviour. This at once rules out the explanation that the 35 per cent. of the thorium-*C* atoms which give short-range α-rays had been separated from the 65 per cent. which give α-rays of long range, because in this case, although radium-*C* disintegrates dually also, all but an infinitesimal fraction of the atoms

[70] R. W. Lawson, *Monatsh.*, 1915, **36**, 845; *A.*, ii, 121.

[71] A. Fleck, *Phil. Mag.*, 1915, [vi], **29**, 337; *A.*, 1915, ii, 131.

[72] *Ann Report*, 1914, 287; S. Loria, *Physikal. Zeitsch.*, 1916, **17**, 6; *Monatsh.*, 1916, **37**, 173; *A.*, ii, 169, 465.

follow one of the two modes. These *C*-members are isotopic with bismuth, and it is probable that, like bismuth, they form several oxides stable within different limits of temperature, which accounts for the discontinuity in the volatilisation curve.

Adsorption of the Radio-elements.

The definite chemical characterisation of all the known radio-elements raises the problem as to how it is they show such definite behaviour in so dilute a solution, and are precipitated, along with other precipitates, at ionic concentrations far below the solubility product. Several papers have been published on this subject.[73] Where the substance carrying down the radio-element is isotopic with it, absorption, of course, can play no special part, for the ratio of the concentrations of the two isotopes in both the solid and liquid phases must be the same, and the ratio of the quantity precipitated to the quantity left in solution also the same for each. Where, however, the two substances are not isotopic, but merely analogous, the radio-element is carried down by the precipitate if under the same conditions it would be precipitated if present in sufficient concentration. The various workers agree on the conclusion that the negative ion governs the precipitation. Adsorption is favoured if the adsorbent has an electronegative constituent, the compound of which with the radio-element is insoluble. Similarly, the addition of an acid containing such an electronegative constituent favours the adsorption. Adsorption in these cases is quite in keeping with the chemical character, whereas in the case of some of the adsorbents first used, such as charcoal, entirely different considerations may apply. An exhaustive study of the adsorption of uranum-X_1 by the last-mentioned substance has shown that the action of the isotope, thorium, in preventing the adsorption, discovered by Ritzel, is shown also by a large number of substances—zirconium salts, benzoic acid, strychnine nitrate, and basic dyes.[74] It was found that a solution of thorium nitrate which has been shaken with charcoal produced afterwards a much smaller effect in preventing the adsorption of uranium-X_1 by charcoal. Similarly, uranium-X_1, freshly produced from uranyl nitrate that has been shaken with charcoal, is more readily adsorbed by charcoal. The authors assume the existence of small quantities of still undiscovered radio-elements in thorium and uranyl nitrates which are the cause of the effect, and are removed when shaken

[73] K. Horovitz and F. Paneth, *Zeitsch. physikal. Chem.*, 1915, **89**, 513; *A.*, 1915, ii, 215; F. Paneth, *Physikal. Zeitsch.*, 1914, **15**, 924; *A.*, 1915, ii, 205; K. Fajans and F. Richter, *Ber.*, 1915, **48**, 700; *A.*, 1915, ii, 405.

[74] H. Freundlich and H. Kaempfer, *Zeitsch. physikal. Chem.*, 1915, **90**, 681; *A.*, ii, 70.

with charcoal. Thorium nitrate, unlike the other substances inhibiting the adsorption, is effective if added to the charcoal after it has adsorbed uranium-X_1, causing the latter to redissolve. It was recognised long ago[75] that, if thorium nitrate did not prevent the adsorption of the isotope uranium-X_1, this means would be available for separating two isotopes, assuming, of course, that the thorium nitrate itself was not, equally with uranium-X_1, adsorbed by the charcoal. The fact that other substances have the same effect as thorium in no way affects this conclusion, but the diminution of the effect of thorium nitrate by shaking the solution with charcoal requires an explanation if these authors' somewhat sweeping assumptions of undiscovered radio-elements is not accepted. Perhaps, to hazard a suggestion, the thorium nitrate itself is more easily absorbed by charcoal after its solution has been shaken with charcoal, which naturally would make it less effective in preventing adsorption of uranium-X_1.

The method of adsorbing radium by colloidal silicic acid, with a view to the subsequent volatilisation of the latter by hydrogen fluoride, has been found unsatisfactory in practice, being very sensitive to the presence of acids and to variations in the character of the silicic acid gel.[76] Manganese dioxide hydrate, prepared either by reducing a permanganate with methyl alcohol or with manganese chloride, has been found suitable, and here it is to be noted the action is chemical, depending on the formation of a radium manganite. An enrichment of the radium from barium may be effected by partial de-adsorption by the electric current, but the best method is to treat the dioxide hydrate with aluminium chloride solution (15 grams of crystallised salt per litre), which replaces more radium than barium in the manganite. It is doubtful from the figures given whether the process is so simple and effective as Mme. Curie's original method of fractionally crystallising the chlorides.

Technical Treatment of Radioactive Materials.

The same authors recommend for the reduction of crude radium residues, consisting mainly of lead and alkaline-earth sulphates, to sulphides soluble in acids, a mixture of calcium hydride and calcium carbide, the latter moderating the violent action of the former.[77] A proportion of one to three suffices for rich residues,

[75] *Ann. Report*, 1910, 275.

[76] *Ibid.*, 1911, 292; E. Ebler and W. Bender, *Zeitsch. angew. Chem.*, 1915, **28**, 25, 41; *A.*, 1913, ii, 659; 1915, ii, 129.

[77] Compare *Ann. Report*, 1913, 277; E. Ebler and W. Bender, *Zeitsch. anorg. Chem.*, 1914, **88**, 255; *A.*, 1915, ii, 404.

but more hydride must be added for the poorer varieties. For the separation and concentration of radium and its isotopes from barium, the fractional precipitation of barium hydroxide from its solution by addition of an alkali hydroxide has been patented.[78] Ionium and actinium have been recovered, from the crude sulphates of the Olary ores, from the filtrate from which the alkaline earths have been separated by sulphuric acid.[79]

Carnotite.—The report of the Bureau of Mines, Washington, Bulletin 104, Mineral Technology 12, dated November, 1915, on the extraction and recovery of radium, uranium, and vanadium from carnotite, contains an interesting account of the steps taken in America to nationalise the extraction of radium. In an experimental plant, from which 4·25 grams of radium (element) were extracted, the cost worked out at 37·6 dollars per milligram, of which 20·71 dollars was the cost of the extraction and the rest the cost of ore. This is on the basis that the uranium and vanadium were not recovered. Actually they were recovered, and it is expected will more than pay the cost of recovery. Full details are given of the factory operations and methods employed, and the report would be invaluable to anyone wishing to start extracting radium technically.

A method which seems promising, previously used in the estimation of radium by the emanation method,[80] has been applied to the extraction of radium from carnotite.[81] Boiling a low-grade ore with 96 per cent. sulphuric acid removed 95 per cent., 78 per cent. sulphuric acid 92 per cent., and 35 per cent. sulphuric acid 42 per cent. of the contained radium, the latter strength sufficing to remove the vanadium and uranium effectively. In actual work with 10 kilogram lots, 18 kilos. of acid, 60° Baumé, containing 78 per cent. of acid, were heated to 190°, and the ore added gradually, with stirring, heating being continued for fifteen minutes at least until the temperature reached 220°. The mixture was filtered on a "Filtros" medium, washed with two lots of fresh hot acid, and the filtrate run into eight times its volume of hot water and well stirred. The radium is precipitated with the barium as sulphate, and in this one operation its concentration is increased more than 230 times. Several per cent. of the radium settles out from the turbid filtrate obtained by washing the residue

[78] H. N. McCoy, *U.S. Pat.*, 1103600, *J. Soc. Chem. Ind.*, 1914, **33**, 919; *A.*, 1915, ii, 3.

[79] S. Radcliff, *J. Roy. Soc. New South Wales*, 1914, **48**, 408; *A.*, 1915, ii, 665.

[80] *Ann. Report*, 1911, 294.

[81] H. Schlundt, *J. Physical Chem.*, 1916, **20**, 485; *A.*, ii, 430.

on the filter with water. An actual recovery of 85 to 95 per cent. of the radium is recorded in four experiments.

A careful investigation of various methods of treating carnotite, noteworthy because all the radio-constituents were traced by α-ray measurements, showed a recovery of 90 per cent. of the uranium and of the radium, 50 per cent. of the polonium, 61 per cent. of the ionium, and 52 per cent. of the actinium.[82] The treatment involved boiling the ore (1) with sodium carbonate to remove the uranium, which separated in a pure form as sodium uranyl carbonate on concentrating the filtered solution; (2) with hydrochloric acid, which removed most of the radium; (3) with nitric acid, some 8 to 10 per cent. more of the radium being obtained; (4) with moderately concentrated sulphuric acid, which removed the ionium. It is interesting that the ionium was not removed in the first three treatments. The residue, which was reduced in weight to one-half that of the mineral, still contained 4·2 per cent. of the initial radium. The carnotite used was not pure, but contained much of its vanadium in a very difficultly attacked form, probably as the silicate, roscoelite. Only part of the vanadium was recovered even by heating the ore in dry hydrogen chloride, when the volatile oxychloride distils away. This method is stated to remove the whole of the vanadium from the crude sodium uranate obtained as a by-product from carnotite.[83] Other methods of effecting the latter separation are (1) the heating of a paste of the uranate and ammonium chloride with water; (2) solution of the uranate in the minimum of dilute acid and boiling, when the vanadium and 13 per cent. of the uranium are precipitated.

Madagascar Minerals.—The districts of Antsirabe and Betafo, Central Madagascar, 100 miles S.W. of Tananarive, is stated to be extraordinarily rich in minerals containing some 20 per cent. of uranium along with columbium, tantalum, and titanium. The complete analyses of four, blomstrandite, betafite, samiresite, ampangabeite, by Lacroix, show 18·1, 26·6, 21·2, and 19·4 per cent. of UO_3 respectively, and also in the second 1·3 and the fourth 2·5 per cent. of thorium oxide.[84] In a new examination of pyromorphite from various sources by radioactive methods,[85] the surface concentration of the radium is denied, and the mineral is stated to be homogeneous as regards its radium content. It is regarded as a young formation, in which radium, deposited at the time of

[82] H. M. Plum, *J. Amer. Chem. Soc.*, 1915, **37**, 1797; *A.*, 1915, ii, 666.

[83] H. H. Barker and H. Schlundt, *J. Soc. Chem. Ind.*, 1916, **35**, 175; *A.*, i, 189.

[84] T. P. Waites, *J. Chem. Met. Min. Soc. S. Africa*, March, 1916, p. 187.

[85] M. Bamberger and G. Weissenberger, *Monatsh.*, 1915, **36**, 169; *A.*, 1915, ii, 506; compare *Ann. Reports*, 1909, 260; 1910, 264.

its formation from the water in which it was formed, has not yet had time to decay.

Artificial Transmutation.

The results to be recorded in this field are all negative. In a series of electric discharge experiments in hydrogen with different sized coils, different types of interrupters, various sized and shaped tubes, with palladium, platinum, and aluminium electrodes, no production of helium or neon was observed,[86] which confirms the view previously taken in these Reports that these gases are not obtained when due precautions against contamination are taken. Uranium oxide subjected to cathode rays lost oxygen to some extent, but there was no evidence that the compound had been rendered more radioactive. Bismuth, similarly treated, was not rendered active, and although it showed subsequently a spectroscopic trace of thallium, this was present also in the untreated metal.[87] Lastly, attempts made to influence the velocity of radioactive transformation by α-rays were unsuccessful, uranium oxide and mesothorium preparations being exposed to the bombardment of the α-rays from the radium emanation without any change in their radioactivity, as subsequently measured, being produced.[88]

Natural Radioactivity.

A radioactive determination of the thorium content of 86 acid, 48 intermediate, and 56 basic rocks gave mean values of 2·1, 1·5, and 0·5 ($\times 10^{-5}$ gram per gram), with a general mean of 1·4.[89] Analyses of the ochre deposited by a strongly radioactive Tyrol spring showed a concentration of radium several times greater than that in the rock from which the water issues, which was a graphite–quartzite containing zircon and about 0·1 per cent. of thorium.[90] A connexion between fertility of the soil and radioactive content was found in the case of thirteen typical Minnesota soils, those richer in radioactive constituents being without exception the more fertile.[91]

A comprehensive survey of the radioactivity of 400 Swedish spring waters showed a relatively high radium content, the most

[86] A. C. G. Egerton, *Proc. Roy. Soc.*, 1915, [A], **91**, 180 ; *A.*, 1915, ii, 132.
[87] W. P. Jorissen and J. A. Vollgraff, *Zeitsch. physikal. Chem.*, 1914, **89**, 151 ; 1915, **90**, 557 ; *A.*, 1915, ii, 134 ; 1916, ii, 71 ; also *A.*, 1915, ii, 664.
[88] J. Danysz and L. Wertenstein, *Compt. rend.*, 1915, **161**, 784 ; *A.*, ii, 69.
[89] J. H. J. Poole, *Phil. Mag.*, 1915, [vi], **29**, 483 ; *A.*, 1915, ii, 207.
[90] G. Weissenberger, *Centr. Min.*, 1914, 481 ; *A.*, 1915, ii, 305.
[91] J. C. Sanderson, *Amer. J. Sci.*, 1915, [iv], **39**, 391 ; *A.*, 1915, ii, 305.

radioactive—up to 172 Mache units—being those from deep borings in the acid rocks—granites and syenites.[92] Two springs, the first in Bloomington, Indiana, and the second at Tuwa, Kaira, Bombay, in which the emanation content varied with the seasonal variation of the flow of the spring, showed precisely opposite behaviour. In the first case the emanation content increased, and in the second case decreased as the flow of the spring increased, suggesting in the latter case a constant supply of total emanation all the year round, independent of flow, and in the former a supply derived from the surrounding soil and depending on the rate of percolation of the water, less decay en route taking place the more rapid the percolation and greater the rainfall.[93]

Obituary.

In conclusion, it is fitting to recall the great losses the science has suffered in the period under review by the deaths of H. G. J. Moseley, in his twenty-eighth year, in the fighting at Suvla Bay, Gallipoli, the youngest investigator, surely, to have won so secure a place in the history of science, and of Sir William Ramsay, who, pre-eminent in chemical science before the discovery of radio-activity, devoted the last ten or twelve years of his vigorous and crowded life more and more exclusively to the young science he did so much to advance.

FREDERICK SODDY.

[92] N. Sahlbom, *Arkiv Kem. Min. Geol.*, 1916, **6**, No. 3, 1; *A.*, ii, 208.
[93] R. R. Ramsay, *Phil. Mag.*, 1915, [vi], **30**, 815; *A.*, ii, 5; A. Steichen, *ibid.*, **31**, 401; *A.*, ii, 284.

ADDENDUM TO FOOTNOTE [4], PAGE 247.

An interesting and important confirmation has just been received through Dr. Lawson, who is interned in Vienna and allowed to work in the Radium Institut under Professor Stefan Meyer. The writer sent Dr. Lawson the first fraction of the above distilled thorite lead, and he now reports (January 31st, 1917) that Professor Hönigschmid has made four determinations of its atomic weight by the silver method, the mean result found being $207{\cdot}77 \pm 0{\cdot}014$, in excellent agreement with the value 207·74 calculated from the relative density of the specimen as found by the writer.

F. S.

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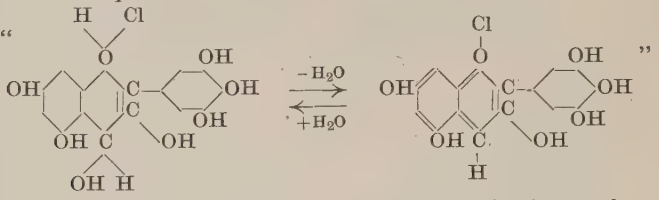
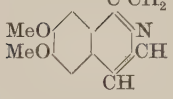


Colourless product. Anthocyanin pigment from myricetin. "

161 3 *for*



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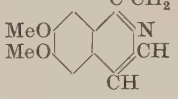
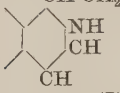
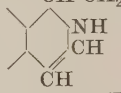


161 12 *for*



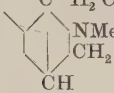
(I).

read



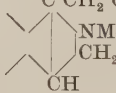
(I).

162 3 *for*



(IV).

read



(IV).

210 11 *after* "'Agriculture' by" *insert* "J. C. Cunningham and W. H. Lancelot; 'Soils and Manures' by"

Annual Reports. Vol. XIII (1916).

Page 172, footnote (39) *for* "A. Davi;" *read* "W. A. Davis."
,, 233, ,, (47) ,, "J. R. Greaves" *read* "J. E. Greaves."
,, 247, line 16* *for* "0·246" *read* "0·26."
,, ,, ,, 5* ,, "0·238" ,, "0·24."
,, 248, ,, 3 ,, "0·246" ,, "0·26."
,, ,, ,, 4 ,, "0·238" ,, "0·24."

* From below.

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